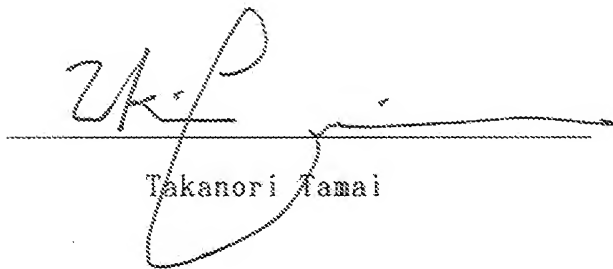


# VERIFICATION OF TRANSLATION

I, Takanori Tamai of TRUST TOWER, 5-36, Miyahara 3-chome, Yodogawa-ku, Osaka-shi, Osaka 532-0003 JAPAN, hereby declare that I am conversant with the Japanese and English languages and that I am the translator of the documents attached and certify that to the best of my knowledge and belief the following is a true and correct English translation of the Japanese Patent Application No. 2003-376183 in the name of NIPPON SHOKUBAI CO.,LTD.

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[Document Name] CLAIMS

[Claim 1]

A cement admixture

5 which comprises a polycarboxylic acid copolymer having  
a polyalkylene glycol side chain essentially including an  
oxyalkylene group containing 3 or more carbon atoms,

said polycarboxylic acid copolymer being constituted of  
two or more species of copolymers with different acid values.

[Claim 2]

10 The cement admixture according to Claim 1,  
wherein the ratio of the acid value of said two or more  
species of copolymers is 1.2 to 5.

[Claim 3]

A cement admixture

15 which comprises a polycarboxylic acid copolymer having  
a polyalkylene glycol side chain containing an oxyalkylene group  
having 3 or more carbon atoms,

said polycarboxylic acid copolymer being constituted of  
two or more species of copolymers with a weight average molecular  
20 weight of 20000 or less.



[Document Name] DESCRIPTION

[Title of the Invention] CEMENT ADMIXTURE

[Technical Field]

[0001]

5           The present invention relates to a cement admixture. More particularly, the present invention relates to a cement admixture which can be suitably used for cement compositions such as cement paste, mortar and concrete.

[Background Art]

10 [0002]

          A cement admixture is widely used as a water-reducing agent for cement compositions such as cement paste, mortar and concrete, and has become essential in constructing civil engineering and building structures and the like from cement compositions. Such  
15 concrete admixtures increase the fluidity of cement compositions to thereby reduce the water requirement of the cement compositions, and therefore are effective in improving the strength, durability and the like, of hardened (cured) products. Among such water reducing agents, polycarboxylic acid concrete  
20 admixtures comprising a polycarboxylic acid copolymer exhibit superior water-reducing performance to naphthalene and other conventional water reducing agents, thus have already led to good results in many cases as high performance AE (air-entraining) and high-range water-reducing admixture.

25 [0003]

          Such cement admixtures are required to be able not only to show water-reducing performance in such cement compositions but also to improve cement compositions in viscosity to thereby facilitate the works at the sites of handling them. Thus, the  
30 cement admixture used as a water-reducing agent are required at the sites of civil engineering and building structure construction and the like not only to be able to show water-reducing performance by decrease in a viscosity of cement compositions but also to provide a viscosity in such the level  
35 that the works will be facilitated at the sites of handling them.

If a cement admixture can exhibit such performance characteristics, it will improve the working efficiency in civil engineering and building structure construction and the like.  
[0004]

5           Meanwhile, regarding a dispersant for an inorganic powder, Patent Document 1, for example, discloses the dispersant containing a water-soluble co-condensate or a water-soluble polymer in which a random polymerization chain (A) of an oxypropylene group and/or an oxybutylene group and an oxyethylene  
10   group is introduced. However, when it is used in cement compositions as an essential components, there was a room for contrivance in order to further improve the working efficiency in a field of the sites of civil engineering and building structure construction and the like, by improving the retaining ability  
15   of fluidity of concrete at a manufacturing field or at the sites of handling them and, at the same time, by improving the condition of concrete so that the workability of concrete becomes excellent.

[Patent Document 1] Japanese Kokai Publication Hei-09-248438  
20   (Page 2)  
[Disclosure of the Invention]  
[Subject which the invention is to Solve]  
[0005]

          The present invention has been made in view of the  
25   above-mentioned state of the art and it is an object of the present invention to provide a cement admixture which can make slump-retaining ability excellent to retain fluidity and, at the same time, can realize a viscosity of cement compositions so that work becomes easy at a field handling them, can make  
30   the state of a cement composition better.  
[0006]

          The present inventors made investigations of a cement admixture retaining fluidity and having excellent workability required in a field of constructing a civil engineering or  
35   construction structure, they paid attention to the fact that

a cement admixture comprising a polycarboxylic acid copolymer having polyalkylene glycol as a side chain can exhibit excellent water-reducing ability in a cement composition. And they found that, by adopting a polyalkylene glycol chain comprising an oxyalkylene group having 3 or more carbon in such the  
5 polycarboxylic acid copolymer, it becomes possible to reduce a viscosity of a cement composition and the like and, by using (1) the copolymer consisting of two or more species of copolymers having different acid values (acid numbers) and/or (2) the  
10 copolymer consisting of two or more species of copolymers having a specified weight average molecular weight as the polycarboxylic acid copolymer comprised in a cement admixture, a cement admixture having excellent properties of respective copolymers can be obtained and the state of a cement composition such as  
15 a concrete which contains the cement admixture becomes better, and slump-retaining ability can be excellent. Thus, they have come to a conclusion that the above-mentioned problems can be solved, which resulted in completion of the present invention. For example, the present inventors found out that dispersing  
20 ability of a cement composition can be improved resulting from a copolymer having larger acid values, slump-retaining ability of a cement composition and the like can be more improved resulting from a copolymer having smaller acid values, and these action effects are combined, thus, a cement composition can be brought  
25 into the state where the work is easy. In addition, since bringing a cement admixture in such the state can make dispersing ability of a cement composition can be improved, it becomes possible to reduce an amount of the cement admixture to be added and improve a compression strength of a hardening product  
30 obtained from a cement composition and the like.

[0007]

That is, the present invention is a cement admixture which comprises a polycarboxylic acid copolymer having a polyalkylene glycol side chain essentially including an oxyalkylene group  
35 containing 3 or more carbon atoms, the polycarboxylic acid

copolymer being constituted of two or more species of copolymers with different acid values.

5 The present invention is also a cement admixture which comprises a polycarboxylic acid copolymer having a polyalkylene glycol side chain containing an oxyalkylene group having 3 or more carbon atoms, said polycarboxylic acid copolymer being constituted of two or more species of copolymers with a weight average molecular weight of 20000 or less.

10 In the following, the present invention is described in detail.  
[0008]

The cement admixture of the present invention comprises a polycarboxylic acid copolymer having a polyalkylene glycol side chain containing an essential oxyalkylene group having 3 or more carbon atoms.

15 The polycarboxylic acid copolymer contains (1) an embodiment of the copolymer constituted of two or more species of copolymers having different acid values and/or (2) an embodiment of the copolymer constituted of two or more species of copolymers with a weight average molecular weight of 20000 or smaller. The copolymer constituted of two or more species of copolymers is a copolymer containing two or more species of copolymers, each of which is assessed as one copolymer by having a particular nature.

25 Incidentally, "a polycarboxylic acid copolymer" means a copolymer suitable for using as a cement admixture, and comprising a polycarboxylic acid or an analogous compound thereof such as the polymer described in this description, for example a derivative or a  
30 polycarboxylic acid salt.

It is preferable that the copolymer is obtained by polymerizing a monomer component containing a polyalkylene glycol unsaturated monomer. More preferably, a monomer component contains an unsaturated carboxylic acid monomer. If  
35 necessary, other copolymerizable monomer may be contained.

When a copolymer is obtained by polymerizing such the monomer component, examples of an embodiment of two or more species of copolymers include (A) an embodiment in which a structure of a polyalkylene glycol chain containing an essential oxyalkylene group having 3 or more carbon atoms is different, (B) an embodiment in which a kind and a use amount of each monomer in a monomer component are different, (C) an embodiment in which a molecular weight of a copolymer obtained by polymerization is different, and (D) a combination of these embodiments. Examples of a structure in the case of (A) include an embodiment in which a polyalkylene glycol side chain containing an essential oxyalkylene group having 3 or more carbon atoms is obtained by random polymerization, an embodiment in which the side chain is obtained by block polymerization, and an embodiment in which the side chain is obtained by alternate polymerization. In addition, in the case of (B), examples include an embodiment in which a kind and a use amount of the aforementioned other copolymerizable monomer are different. Such the two or more kind of copolymers can be obtained by preparing separately two or more species of copolymers, and then, mixing those copolymers, or preparing so that two or more species of copolymers are produced.

[0009]

In the embodiment of (1), when the polycarboxylic acid copolymer is constructed of two or more species of copolymers having different acid values, acid values of these copolymers are different and, when the polycarboxylic acid copolymer is constructed of three or more species of copolymers, an embodiment may be an embodiment in which an acid value of respective copolymers are different, or an embodiment in which at least two species of copolymers having the same acid value are contained.

[0010]

It is preferable that the ratio of the acid value of the aforementioned two or more species of copolymers is 1.2 to 5.

When the ratio is less than 1.2, or exceeds 5, there is a possibility that dispersity of a cement composition and slump-retaining ability can not be sufficiently improved. A lower limit value is more preferably 1.3, and still more preferably 1.5. An upper limit value is more preferably 4, and still more preferably 3. More preferably, the range is 1.3 to 4, and still more preferably 1.5 to 3.

When the aforementioned copolymers is two species, representing larger acid values as "A" and smaller acid values as "B", the aforementioned ratio of the acid value is "A/B" and, when the aforementioned copolymers is three species or more, representing the largest acid value among them "C" and the smallest acid value "D", the ratio is "C/D".

[0011]

Regarding respective acid values of the aforementioned two or more species of copolymers, for a copolymer having the largest acid value, a lower limit value is preferably 10%, more preferably 12%, and still more preferably 15%. An upper limit value is preferably 40%, more preferably 35%, and still more preferably 30%. In addition, a preferable range is 10 to 40%, more preferably 12 to 35%, and still more preferably 15 to 30%. When an acid value is less than 10%, or exceeds 40%, there is a possibility that dispersity of a cement composition is not sufficiently improved. In a copolymer having the lowest acid value, a lower limit value is preferably 5%, more preferably 7%, and still more preferably 8%. An upper limit value is preferably 30%, more preferably 25%, and still more preferably 20%. In addition, a preferable range is 5 to 30%, more preferably 7 to 25%, and still more preferably 8 to 20%. When the amount is less than 5%, or exceeds 30%, there is a possibility that slump-retaining ability of a cement composition is not sufficiently improved.

[0012]

The aforementioned acid value means a ratio (%) of a monomer having an acid group and/or a group obtained by neutralizing

the acid group in a monomer component. For example, when the copolymer is obtained by polymerizing a monomer component, representing a mixing weight of a monomer having an acid group in the monomer component as "a", and representing a mixing weight  
5 of a monomer not having an acid group as "b", an acid value "A" can be obtained by the following equation:

$$\text{Acid value "A"} = 100 \times a / (a+b)$$

For example, in the case where the total monomer component amount is assumed to be 100% by weight (weight%, mass% or % by mass), when the monomer component consists of 75% by weight of  
10 a polyalkylene glycol monomer, and 25% by weight of methacrylic acid having a carboxyl group as an acid group, an acid value is 25%. When the monomer component consists of 60% by weight of a polyalkylene glycol monomer, 30% by weight of methacrylic  
15 acid and 10% by weight of methyl methacrylate, an acid value is 30%.

As the acid group, a carboxyl group, and a sulfonic acid group are suitable examples. The "a group obtained by neutralizing the acid group " means a group where a hydrogen  
20 ion that can be dissociated of the acid group is substituted with another cation.

[0013]

A weight average molecular weight of each of two or more kinds of copolymers in the embodiment of the above (1) is  
25 preferably 1000 or larger in terms of polyethylene glycol by GPC. The weight average molecular weight is more preferably 3,000 or larger, still more preferably 5,000 or larger, and particularly preferably 7,000 or larger. And, the weight average molecular weight is preferably 500,000 or smaller, more  
30 preferably 300,000 or smaller, still more preferably 100,000 or smaller, and particularly preferably 80,000 or smaller. When the weight average molecular weight is smaller than 1,000, or exceeds 500,000, there is a possibility that dispersity is reduced.

35 [0014]

In the embodiment of the above (2), when a weight average molecular weight of at least one kind of two or more kinds of copolymers exceeds 20,000, slump-retaining ability of a cement composition can not be sufficiently improved, and a cement composition can not be brought into the state where work is sufficiently easy. A weight average molecular weight is preferably 19,000 or smaller, more preferably 18,000 or smaller.

The above mentioned weight average molecular weight can be determined by gel permeation chromatography (hereinafter referred to as "GPC") and expressed on the polyethylene glycol equivalent. For example it can be determined by the following measurement conditions.

[0015]

[GPC molecular weight measurement conditions]

Column used: Tosoh TSK guard column SWXL + TSK gel G4000SWXL + G3000SWXL + G2000SWXL

Eluent: Sodium acetate trihydrate (115.6 g) is dissolved in a mixed solvent composed of 10999 g of water and 6001 g of acetonitrile, and the solution is further adjusted to pH 6.0 with acetic acid and used as the solution of the eluent.

Injection volume: 100  $\mu$ L of the 0.5% solution of the eluent

Eluent flow rate: 0.8 mL/min

Column temperature: 40°C

Standard samples: Polyethylene glycol, peak-top molecular weights (Mp) 272500, 219300, 85000, 46000, 24000, 12600, 4250, 7100, 1470

Order of Calibration curve: 3rd-order

Detector: Waters, Japan's 410 differential refractive index detector

Analysis software: Waters, Japan's MILLENNIUM Ver. 3.21

[0016]

The cement admixture of the present invention contains a polycarboxylic acid copolymer having a polyalkylene glycol side chain containing an essential oxyalkylene group having 3 or more carbon atoms, and may contain a polymer other than such



the copolymer. In the case where the total polymer amount contained in the cement admixture of the present invention is assumed to be 100% by weight, a content of a polycarboxylic acid copolymer having a polyalalkylene glycol side chain containing an essential oxyalkylene group having 3 or more carbon atoms is preferably 50% by weight or larger. When the content is less than 50% by weight, there is a possibility that dispersity of a cement composition can not be sufficiently improved. The content is preferably 60% by weight or larger, and still more preferably 70% by weight or larger.

[0017]

Regarding an acid value of a total polymer contained in the cement admixture, a lower limit value is preferably 20 mgKOH/g, more preferably 40 mgKOH/g, and still more preferably 60 mgKOH/g. An upper limit value is preferably 140 mgKOH/g, more preferably 120 mgKOH/g, and still more preferably 100 mgKOH/g. In addition, a preferably range is 20 to 140 mgKOH/g, more preferably 40 to 120 mgKOH/g, and still more preferably 60 to 100 mgKOH/g. When an acid value is less than 20 mgKOH/g, there is a possibility that cement dispersing performance is remarkably reduced. When an acid value exceeds 140 mgKOH/g, there is a possibility that slump-retaining ability is remarkably reduced.

[0018]

The acid value means an amount (mgKOH/g) of potassium hydroxide consumed by neutralization when 1g of a polymer is neutralized with potassium hydroxide (KOH). For example, the acid value can be obtained as follows:

[Method of measuring acid value]

80 ml of acetone and 10 ml of water were added to 0.5 to 1g of a solution of a polymer whose acid value is sought to obtain, they are stirred to uniformly dissolve, a solution is titrated with an automated titration apparatus ("COM-555" manufactured by Hiranuma Sangyo) using an 0.1 mol/L KOH aqueous solution as a titration solution to measure an acid value of a solution.

On the other hand, 2 ml of acetone is added to 1.0 g of the

aforementioned polymers solution to dissolve the polymer to obtain a solution. The solution is subsequently naturally dried at a normal temperature, dried for 5 hours under reduced pressure (160°C /5 mmHg), then allowed to cool in a desiccator, and a weight is measured. Thereafter, an acid value (mgKOH/g) of a polymer is calculated from an acid value of a solution and a resin solid matter of a solution.

[0019]

When the cement admixture of the present invention is used, a flow stop value of a concrete is preferably 15 seconds or shorter. When the value exceeds 15 seconds, there is a possibility that work can not be sufficiently done at a field handling a cement composition. The value is more preferably 14 seconds or shorter, and still more preferably 13 seconds or shorter.

The flow stop value can be measured as follows:

A concrete having the following composition is prepared, a cement admixture is added at about 0.25% by weight relative to 100% by weight of a concrete, an amount of an air is adjusted to 3 to 4%, and the time required from a point that a slump cone is pulled up to a point that fluidization of concrete was stopped when an initial (0 min) slump flow value is measured to obtain the flow stop value. Measurement of the slump flow value and an amount of the air can be performed according to Japanese Industrial Standards (JIS A 1101, 1128, 6204).

[Concrete formulation]

Water: 172 kg/m<sup>3</sup>

Cement (manufactured by Taiheiyo Cement, manufactured by Sumitomo Osaka Cement, manufactured by Ube Mitsubishi Cement: normal portland Cement): 491 kg/m<sup>3</sup>

Fine filler (Ohigawa river sand) : 744.5 kg/m<sup>3</sup>

Clued filler (Aoume-produced ground stone) : 909.8 kg/m<sup>3</sup>

W/C : 35%

[0020]

As described above, it is preferable that a copolymer in the present invention is obtained by polymerizing a polyalkylene

glycol unsaturated monomer as a monomer component. In addition, it is preferable that the copolymer contains an unsaturated carboxylic acid monomer as a monomer component and, if necessary, may contain a monomer copolymerizable with the monomer.

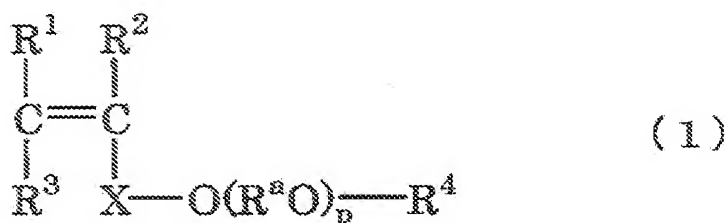
5 When the copolymer is a salt of a carboxylic acid, for example, an alkali metal salt, an alkaline earth metal salt and an ammonium salt are used. Alternatively, a monomer as a carboxylic acid salt may be polymerized, or a monomer of carboxylic acid may be polymerized and, thereafter, a salt may  
10 be formed.

A ratio of a polyalkylene glycol unsaturated monomer and an unsaturated carboxylic acid monomer to be contained in the monomer component is 0.1 or more, preferably 2 or less, more preferably 0.3 or more and 1.2 or less, as expressed by  
15 polyalkylene glycol unsaturated monomer/unsaturated carboxylic acid monomer (mole ratio).

[0021]

It is preferable that the polyalkylene glycol unsaturated monomer contains an essential oxyalkylene group having 3 or more  
20 carbon atoms. As such the polyalkylene glycol unsaturated monomer, for example, a monomer represented by the following formula (1) is preferable.

[0022]



25 [0023]

In the above formula (1),  $\text{R}^1$ ,  $\text{R}^2$  and  $\text{R}^3$  are the same or different and each represents a hydrogen atom or a methyl group.  $\text{R}^4$  represents a hydrogen atom or a hydrocarbon group containing 1 to 30 carbon atoms.  $\text{R}^a$  may be the same or different and each  
30 represents an alkylene group containing 2 to 18 carbon atoms,

and  $R^a$  is containing 3 or more carbons at least one alkylene group.  $p$  represents the average molar number of addition of the oxyalkylene group and is a number of 1 to 300.  $X$  represents divalent alkylene group containing 1 to 5 carbon atoms or  
 5 represents that  $-CO-$  bond or  $-R^b-CO-$  bond or direct bond. In case  $X$  represents the direct bond, the carbon atom and oxygen atom bonded thereto are directly bond to each other.  $R^b$  represents divalent alkylene group containing 1 to 5 carbon atoms.

10 [0024]

At least one species of oxyalkylene group represented by  $-(R^aO)-$  in the above formula (1) is oxyalkylene group which containing 3 or more carbon atoms.

In cases where two or more oxyalkylene group occur in the same  
 15 monomer, the oxyalkylene groups represented by  $-(R^aO)-$  may be in any addition embodiment, namely random addition, block addition, alternate addition or the like.

The oxyalkylene group(s) represented  $-(R^aO)-$  as mentioned above is an alkylene oxide adduct which consists of alkylene  
 20 oxide groups containing 2 to 18 carbon atoms. And at least one alkylene oxide containing 3 or more carbons is added to. Such alkylene oxide adduct has a structure formed by one or two or more of alkylene oxides such as ethylene oxide, propylene oxide, butylene oxide, isobutylene oxide, 1-butene oxide and 2-butene  
 25 oxide. Among such alkylene oxide adducts, propylene oxide and butylene oxide adducts are preferred. Still more preferably, the structure contains an addition of ethylene oxides.

In other word, it is more preferably that the structure contains oxypropylene group and /or oxybutylene group as  
 30 essential constituents, and oxyethylene group. In this case, it contains 50 to 95mol% of oxyethylene group relative to 100mol% of all the oxyalkylene group. If it is less than 50 mole %, the hydrophilicity of the oxyalkylene groups may possibly become insufficient to decrease dispersing ability of cement particles.  
 35 More preferably not less than 60mol%, still more preferably not

less than 70mol%, especially more preferably not less than 80mol%, most preferably not less than 90mol%.

[0025]

The average molar number  $p$  of addition of oxyalkylene groups represented by the above  $R^aO$  is a number of 1 to 300. If  $p$  exceeds 300, the polymerizability of the monomer will decrease.

To obtain excellent fluidity, a preferred range of  $p$  is not less than 3 but not more than 280. More preferably,  $m$  is not less than 5, still more preferably not less than 10, especially preferably not less than 20. On the other hand,  $p$  is more preferably not more than 250, especially preferably not more than 150.

For preparing concrete compositions low in viscosity, as for the range of  $p$ , it is preferably not less than 3, more preferably not less than 4, still more preferably not more than 5. On the other hand, it is preferably not more than 100, more preferably not more than 50, still more preferably not more than 30, especially preferably not more than 25.

[0026]

In  $-(R^aO)_p-$  in the above formula (1), as for the average molar number of addition of the oxyalkylene group containing 3 or more carbon atoms, it is preferably not less than 0.2, more preferably not less than 0.5 but not more than 10. Still more preferably, it is not less than 1 but not more than 7. Setting the average molar number of addition in such a range, it may decrease the viscosity of cement composition or like well enough.

As for the average molar number of addition of the oxyalkylene group(s), it is preferably not less than 2. If the average molar number of addition of the oxyethylene group(s) is less than 2, it may not obtain enough hydrophilic property to disperse cement particles or like and may not obtain the excellent fluidity.

More preferably not less than 3, still more preferably not less than 5, especially preferable not less than 10. On

the other hand, more preferably not more than 280, still more preferably not more than 250, especially preferably not more than 200, most preferably not more than 150.

5 The average molar number of addition means the average value for the molar number of the oxyalkylene group(s) in one mole of group formed by oxyalkylene group.

[0027]

It is possible to use, as said monomer represented by formula (1) mentioned above, a combination of two or more monomer species differing in the average molar number  $p$  of addition of the oxyalkylene group(s). As a suitable combination, there may be mentioned, for example, a combination of two monomer species differing the average molar number  $p$  of addition by not more than 10 (preferably a difference in  $p$  by not more than 5), a combination of two monomer species differing in the average molar number  $p$  of addition by not less than 10 (preferably a difference in  $p$  by not less than 15), or a combination of not less than three monomer species differing in  $p$  by not less than 10 (preferably a difference in  $p$  by not less than 15) from one another.

10 Furthermore, as for the range of  $p$  for combined use, it is possible to combine a monomer having an average molar number  $p$  of addition in the range of 40 to 300 with a monomer having the range of 1 to 40 (the difference in  $p$  being not less than 10, preferably not less than 15), or combine a monomer having an average molar number  $p$  of addition in the range of 20 to 300 with a monomer having the range of 1 to 20 (the difference in  $p$  being not less than 10, preferably not less than 15).

15 20 25

[0028]

In case the monomer is polyalkylene glycol ester monomer represented by above mentioned formula (1), as for oxyalkylene group represented by  $-(R^A O)_p-$ , from the viewpoint of esterification productivity improvement with (meth)acrylic acid, it is preferred that the ethylene oxide moiety be added to the site of the ester bond with (meth)acrylic acids monomer

30 35

$(R^1 R^3 C = CR^2 - COOH)$ .

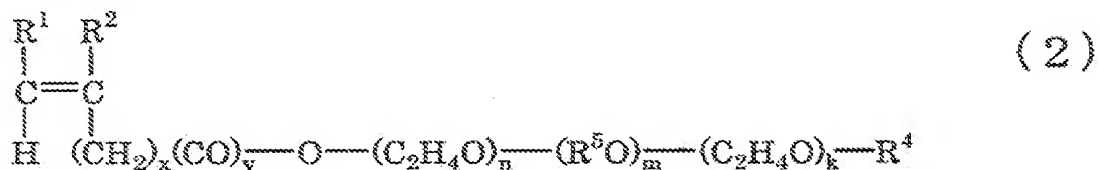
[0029]

When a carbon number of the  $R^4$  exceeds 30, since hydrophobicity of the cement admixture of the present invention becomes too strong, there is a possibility that better dispersity cannot be obtained. From a viewpoint of dispersity, a preferable embodiment of  $R^4$  is a hydrocarbon group having 1 to 20 carbon atom(s) or hydrogen, more preferably a hydrocarbon group having 10 or less carbon atom(s), still more preferably a hydrocarbon group having 5 or less carbon atom(s), still more preferably a hydrocarbon group having 3 or less carbon atom(s), and particularly preferably a hydrocarbon group having 2 or less carbon atom(s). Among a hydrocarbon group, a saturated alkyl group and an unsaturated alkyl group are preferable. These alkyl groups may be straight or branched. In addition, in order to manifest excellent material separation preventing performance, and make an amount of the air brought in a cement composition appropriate, a hydrocarbon group having 5 or more carbon atoms is preferable, and a hydrocarbon group having 20 or less carbon atoms is preferable. More preferable is a hydrocarbon group having 5 to 10 carbon atoms. Among a hydrocarbon group, a saturated alkyl group and an unsaturated alkyl group are preferable. These alkyl groups may be straight or branched.

[0030]

When there are two or more kinds of oxyalkylene groups in the same monomer as described above, the aforementioned polyalkylene glycol unsaturated monomer may be any addition form of an oxyalkylene group represented by  $-(R^aO)-$  such as random addition, block addition and alternate addition. For example, in the case of a form of block addition, a monomer represented by the following formula (2) is preferable.

[0031]



[0032]

In the formula,  $R^1$  and  $R^2$  are the same or different, and represent a hydrogen atom or a methyl group.  $R^3$ s are the same or different, and represent an alkylene group having 3 to 18 carbon atoms. And, x represents a number of 0 to 2, y represents 0 or 1, n and k represent an average molar number of addition of an oxyethylene group, n is a number of 1 to 200, k is a number of 1 to 200, m represents an average molar number of addition of an oxyalkylene group, and is a number of 1 to 50, and  $n+m+k$  is a number of 3 to 200.  $R^4$  represents a hydrogen atom or a hydrocarbon group having 1 to 20 carbon atom(s).

[0033]

In the formula (2), n and k may be the same or different, and are a number of 1 to 200. When they exceed 200, a viscosity is increased, and workability is inferior in some cases, and they are preferably 1 to 60, and more preferably 1 to 20. m is a number of 1 to 50 and, when m1 exceeds 50, water-reducing property is reduced, hydrophobicity is increased, an admixture is not compatible with mixing water to be added to a cement, and workability is inferior in some cases. A range of m is preferably 1 to 20, more preferably 1 to 5, and still more preferably 1 to 3. And,  $n+m+k$  which is a sum of n, m and k is a number of 3 to 200. And when this exceeds 200, a viscosity is increased, and workability is inferior in some cases, and the sum is preferably 5 to 120, more preferably 5 to 100, and still more preferably 5 to 50.  $R^5$ s may be the same or different, and represent an alkylene group having 3 to 18 carbon atoms, and it is preferably a 2-methylethylene group having 3 carbon atoms (generally, a precursor thereof is propylene oxide).  $R^4$  represents a hydrogen atom or a hydrocarbon group having 1 to 20 carbon atom(s), preferably a methyl group.

[0034]

A monomer represented by the formula (2) can be obtained by adding ethylene oxide in a proper amount so as to give the prescribed repeating number to an unsaturated alcohol or an



unsaturated carboxylic acid; adding alkylene oxide containing 3 to 18 carbon atoms in a proper amount so as to give the prescribed repeating number; and adding ethylene oxide in a proper amount so as to give the prescribed repeating number. Furthermore, the monomer can also be obtained by esterification of an alcohol, which is obtained by adding ethylene oxide in a proper amount so as to give the prescribed repeating number to an alcohol or a phenol comprising a hydrocarbon group containing 1 to 20 carbon atoms, adding alkylene oxide of 3 to 18 carbon atoms in a proper amount so as to give the prescribed repeating number, and adding ethylene oxide in a proper amount so as to give the prescribed repeating number, with an unsaturated carboxylic acid or ester exchange reaction of the alcohol with an unsaturated carboxylic acid ester.

[0035]

As the unsaturated alcohol, it is preferable that vinyl alcohol, allyl alcohol, methallyl alcohol, 3-butene-1-ol, 3-methyl-3-butene-1-ol, 3-methyl-2-butene-1-ol, 2-methyl-3-butene-2-ol, 2-methyl-2-butene-1-ol, 2-methyl-3-butene-1-ol and the like. As unsaturated carboxylic acid, acrylic acid and methacrylic acid are preferable. Further, as unsaturated carboxylic acid ester, alkylester of these unsaturated carboxylic acids can be used. As alkylene oxide having 3 to 18 carbon atoms, propylene oxide, butylene oxide, and an epoxylated unsaturated hydrocarbon are preferable. Among them, propylene oxide is preferable.

As the aforementioned alcohol or phenol having a hydrocarbon group having 1 to 20 carbon atom(s), alkyl alcohol such as methanol, ethanol, and butanol; alcohol having an aryl group such as benzyl alcohol; phenols such as phenol and paramethylphenol are preferable. Among them, alcohol of a carbon number of 1 to 3 such as methanol, ethanol and butanol is preferable.

[0036]

A ratio of a monomer unit formed by a compound represented

by the formula (2) relative to a total weight of the copolymer is preferably 10 to 95% by weight, more preferably 50 to 90% by weight, and still more preferably 65 to 85% by weight. In addition, when the copolymer is obtained by copolymerizing a monomer (X) represented by the formula (2) and an unsaturated carboxylic acid monomer (Y), relative to 100% by weight of the total weight of (X) and (Y), (X) is preferably 10 to 95% by weight, more preferably 50 to 90% by weight, and still more preferably 65 to 85% by weight. In addition, a copolymerizable monomer other than (X) and (Y) may be used as a copolymerizable composition and, relative to 100% by weight of the total weight of (X) and (Y), an amount of the monomer to be used is 0 to 50% by weight. [0037]

A monomer not having an oxyalkylene group having 3 or more carbon atoms may be used jointly with the polyalkylene glycol unsaturated monomer. That is, a monomer in which an oxyalkylene group represented by  $-(R^aO)-$  in the formula (1) is all an oxyethylene group may be used. Such the polyalkylene glycol unsaturated monomer is the same except that an oxyalkylene group having 3 or more carbon atoms does not contain in the aforementioned polyalkylene glycol unsaturated monomer. [0038]

Suited as the polyalkylene glycol unsaturated monomer, that is, a polyalkylene glycol unsaturated monomer having an oxyalkylene group having 3 or more carbon atoms and a polyalkylene glycol unsaturated monomer not having an oxyalkylene group having 3 or more carbon atoms are, for example, an unsaturated alcohol-polyalkylene glycol adduct and a polyalkylene glycol ester monomer.

The above-mentioned unsaturated alcohol-polyalkylene glycol adduct may be any compounds that have a structure in which a polyalkylene glycol chain is added to an alcohol containing an unsaturated group. The above mentioned polyalkylene glycol ester monomer may be any of monomers that have a structure in which an unsaturated group is bonded to a polyalkylene glycol

chain via an ester bond. Preferred is an unsaturated carboxylic acid polyalkylene glycol ester compound, and particularly preferred is (alkoxy)polyalkylene glycol mono(meth)acrylate. [0039]

5           Suitable as the above-mentioned unsaturated alcohol-polyalkylene glycol adduct are, for example, a vinyl alcohol-alkylene oxide adduct, (meth)allyl alcohol-alkylene oxide adduct, 3-buten-1-ol-alkylene oxide adduct, isoprene alcohol (3-methyl-3-buten-1-ol)-alkylene oxide adduct, 10 3-methyl-2-buten-1-ol-alkylene oxide adduct, 2-methyl-3-buten-2-ol-alkylene oxide adduct, 2-methyl-2-buten-1-ol-alkylene oxide adduct, 2-methyl-3-buten-1-ol-alkylene oxide adduct and the like. [0040]

15           Suitable as the above-mentioned unsaturated alcohol-polyalkylene glycol adduct are also polyethylene glycol monovinyl ether, methoxy polyethylene glycol monovinyl ether, polyethylene glycol mono(meth)allyl ether, methoxy polyethylene glycol mono(meth)allyl ether, polyethylene glycol 20 mono(2-methyl-2-propenyl) ether, polyethylene glycol mono(2-butenyl) ether, polyethylene glycol mono(3-methyl-3-butenyl) ether, polyethylene glycol mono(3-methyl-2-butenyl) ether, polyethylene glycol mono(2-methyl-3-butenyl) ether, polyethylene glycol 25 mono(2-methyl-2-butenyl) ether, polyethylene glycol mono(1,1-dimethyl-2-propenyl) ether, polyethylene-polypropylene glycol mono(3-methyl-3-butenyl) ether, methoxypolyethylene glycol mono(3-methyl-3-butenyl) ether, ethoxypolyethylene glycol mono(3-methyl-3-butenyl) 30 ether, 1-propoxypolyethylene glycol mono(3-methyl-3-butenyl) ether, cyclohexyloxypolyethylene glycol mono(3-methyl-3-butenyl) ether, 1-octyloxypolyethylene glycol mono(3-methyl-3-butenyl) ether, nonylalkoxypolyethylene glycol mono(3-methyl-3-butenyl) ether, 35 laurylalkoxypolyethylene glycol mono(3-methyl-3-butenyl)

ether, stearylalkoxypolyethylene glycol  
 mono(3-methyl-3-butenyl) ether, phenoxypolyethylene glycol  
 mono(3-methyl-3-butenyl) ether, naphthoxypolyethylene glycol  
 mono(3-methyl-3-butenyl) ether, methoxypolyethylene glycol  
 5 monoallyl ether, ethoxypolyethylene glycol monoallyl ether,  
 phenoxypolyethylene glycol monoallyl ether,  
 methoxypolyethylene glycol mono(2-methyl-2-propenyl) ether,  
 ethoxypolyethylene glycol mono(2-methyl-2-propenyl) ether,  
 phenoxypolyethyleneglycol mono(2-methyl-2-propenyl) ether and  
 10 the like.

[0041]

The above-mentioned (alkoxy)polyalkylene glycol  
 mono(meth)acrylate may be the one mentioned above, but suitable  
 are esterification products of (meth)acrylic acid with  
 15 alkoxypolyalkylene glycols, especially preferably  
 alkoxypolyalkyleneglycols which are mainly formed of an ethylene  
 oxide group(s), obtained by addition of 1 to 300 moles of an  
 alkylene oxide group(s) containing 2 to 18 carbon atoms to any  
 of aliphatic alcohols containing 1 to 30 carbon atoms such as  
 20 methanol, ethanol, 1-propanol, 2-propanol, 1-butanol,  
 2-butanol, 1-pentanol, 2-pentanol, 3-pentanol, 1-hexanol,  
 2-hexanol, 3-hexanol, octanol, 2-ethyl-1-hexanol, nonyl  
 alcohol, lauryl alcohol, cetyl alcohol and stearyl alcohol;  
 alicyclic alcohols containing 3 to 30 carbon atoms such as  
 25 cyclohexanol; and unsaturated alcohols containing 3 to 30 carbon  
 atoms such as (meth)allyl alcohol, 3-buten-1-ol and  
 3-methyl-3-buten-1-ol.

[0042]

Suitable as said esterification products are those  
 30 (alkoxy)polyethylene glycol (poly) (alkylene glycol containing  
 2 to 4 carbon atoms) (meth)acrylates which are given below:  
 Methoxypolyethylene glycol mono(meth)acrylate,  
 methoxy{polyethylene glycol-(poly)propylene glycol}  
 mono(meth)acrylate, methoxy{polyethylene  
 35 glycol-(poly)butylene glycol} mono(meth)acrylate,

methoxy{polyethylene glycol-(poly)propylene  
 glycol-(poly)butylene glycol} mono(meth)acrylate,  
 ethoxypolyethylene glycol mono(meth)acrylate,  
 ethoxy{polyethylene glycol-(poly)propylene glycol}  
 5 mono(meth)acrylate, ethoxy{polyethylene  
 glycol-(poly)butylene glycol} mono(meth)acrylate,  
 ethoxy{polyethylene glycol-(poly)propylene  
 glycol-(poly)butylene glycol} mono(meth)acrylate,  
 propoxypolyethylene glycol mono(meth)acrylate,  
 10 propoxy{polyethylene glycol-(poly)propylene glycol}  
 mono(meth)acrylate, propoxy{polyethylene  
 glycol-(poly)butylene glycol} mono(meth)acrylate,  
 propoxy{polyethylene glycol-(poly)propylene  
 glycol-(poly)butylene glycol} mono(meth)acrylate,  
 15 [0043]  
 butoxypolyethylene glycol mono(meth)acrylate,  
 butoxy{polyethylene glycol-(poly)propylene glycol}  
 mono(meth)acrylate, butoxy{polyethylene  
 glycol-(poly)butylene glycol} mono(meth)acrylate,  
 20 butoxy{polyethylene glycol-(poly)propylene  
 glycol-(poly)butylene glycol} mono(meth)acrylate,  
 pentoxypolyethylene glycol mono(meth)acrylate,  
 pentoxy{polyethylene glycol-(poly)propylene glycol}  
 mono(meth)acrylate, pentoxy{polyethylene  
 25 glycol-(poly)butylene glycol} mono(meth)acrylate,  
 pentoxy{polyethylene glycol-(poly)propylene  
 glycol-(poly)butylene glycol} mono(meth)acrylate,  
 hexoxypolyethylene glycol mono(meth)acrylate,  
 hexoxy{polyethylene glycol-(poly)propylene glycol}  
 30 mono(meth)acrylate, hexoxy{polyethylene  
 glycol-(poly)butylene glycol} mono(meth)acrylate,  
 hexoxy{polyethylene glycol-(poly)propylene  
 glycol-(poly)butylene glycol} mono(meth)acrylate,  
 [0044]  
 35 heptoxypolyethylene glycol mono(meth)acrylate,

heptoxy{polyethylene glycol-(poly)propylene glycol}  
mono(meth)acrylate, heptoxy{polyethylene  
glycol-(poly)butylene glycol} mono(meth)acrylate,  
heptoxy{polyethylene glycol-(poly)propylene  
5 glycol-(poly)butylene glycol} mono(meth)acrylate,  
octoxypolyethylene glycol mono(meth)acrylate,  
octoxy{polyethylene glycol-(poly)propylene glycol}  
mono(meth)acrylate, octoxy{polyethylene  
glycol-(poly)butylene glycol} mono(meth)acrylate,  
10 octoxy{polyethylene glycol-(poly)propylene  
glycol-(poly)butylene glycol} mono(meth)acrylate,  
nonanoxypolyethylene glycol mono(meth)acrylate,  
nonanoxypolyethylene glycol-(poly)propylene glycol}  
mono(meth)acrylate, nonanoxypolyethylene  
15 glycol-(poly)butylene glycol} mono(meth)acrylate,  
nonanoxypolyethylene glycol-(poly)propylene  
glycol-(poly)butylene glycol} mono(meth)acrylate,  
[0045]  
decanoxypolyethylene glycol mono(meth)acrylate,  
20 decanoxypolyethylene glycol-(poly)propylene glycol}  
mono(meth)acrylate, decanoxypolyethylene  
glycol-(poly)butylene glycol} mono(meth)acrylate,  
decanoxypolyethylene glycol-(poly)propylene  
glycol-(poly)butylene glycol} mono(meth)acrylate,  
25 undecanoxypolyethylene glycol mono(meth)acrylate,  
undecanoxypolyethylene glycol-(poly)propylene glycol}  
mono(meth)acrylate, undecanoxypolyethylene  
glycol-(poly)butylene glycol} mono(meth)acrylate,  
undecanoxypolyethylene glycol-(poly)propylene  
30 glycol-(poly)butylene glycol} mono(meth)acrylate,  
dodecanoxypolyethylene glycol mono(meth)acrylate,  
dodecanoxypolyethylene glycol-(poly)propylene glycol}  
mono(meth)acrylate, dodecanoxypolyethylene  
glycol-(poly)butylene glycol} mono(meth)acrylate,  
35 dodecanoxypolyethylene glycol-(poly)propylene

glycol-(poly)butylene glycol} mono(meth)acrylate,  
[0046]

tridecanoxypolyethylene glycol mono(meth)acrylate,  
tridecanoxy{polyethylene glycol-(poly)propylene glycol}  
5 mono(meth)acrylate, tridecanoxy{polyethylene  
glycol-(poly)butylene glycol} mono(meth)acrylate,  
tridecanoxy{polyethylene glycol-(poly)propylene  
glycol-(poly)butylene glycol} mono(meth)acrylate,  
tetradecanoxypolyethylene glycol mono(meth)acrylate,  
10 tetradecanoxy{polyethylene glycol-(poly)propylene glycol}  
mono(meth)acrylate, tetradecanoxy{polyethylene  
glycol-(poly)butylene glycol} mono(meth)acrylate,  
tetradecanoxy{polyethylene glycol-(poly)propylene  
glycol-(poly)butylene glycol} mono(meth)acrylate,  
15 pentadecanoxypolyethylene glycol mono(meth)acrylate,  
pentadecanaboxy{polyethylene glycol-(poly)propylene glycol}  
mono(meth)acrylate, pentadecanoxy{polyethylene  
glycol-(poly)butylene glycol} mono(meth)acrylate,  
pentadecanoxy{polyethylene glycol-(poly)propylene  
20 glycol-(poly)butylene glycol} mono(meth)acrylate,  
[0047]

hexadecanoxypolyethylene glycol mono(meth)acrylate,  
hexadecanoxy{polyethylene glycol-(poly)propylene glycol}  
mono(meth)acrylate, hexadecanoxy{polyethylene  
25 glycol-(poly)butylene glycol} mono(meth)acrylate,  
hexadecanoxy{polyethylene glycol-(poly)propylene  
glycol-(poly)butylene glycol} mono(meth)acrylate,  
heptadecanoxypolyethylene glycol mono(meth)acrylate,  
heptadecanoxy{polyethylene glycol-(poly)propylene glycol}  
30 mono(meth)acrylate, heptadecanoxy{polyethylene  
glycol-(poly)butylene glycol} mono(meth)acrylate,  
heptadecanoxy{polyethylene glycol-(poly)propylene  
glycol-(poly)butylene glycol} mono(meth)acrylate,  
octadecanoxypolyethylene glycol mono(meth)acrylate,  
35 octadecanoxy{polyethylene glycol-(poly)propylene glycol}

mono(meth)acrylate, octadecanoxy{polyethylene glycol-(poly)butylene glycol} mono(meth)acrylate, octadecanoxy{polyethylene glycol-(poly)propylene glycol-(poly)butylene glycol} mono(meth)acrylate,

5 [0048]

nonadecanoxypolyethylene glycol mono(meth)acrylate, nonadecanoxy{polyethylene glycol-(poly)propylene glycol} mono(meth)acrylate, nonadecanoxy{polyethylene glycol-(poly)butylene glycol} mono(meth)acrylate, 10 nonadecanoxy{polyethylene glycol-(poly)propylene glycol-(poly)butylene glycol} mono(meth)acrylate, cyclopentoxypolyethylene glycol mono(meth)acrylate, cyclopentoxy{polyethylene glycol-(poly)propylene glycol} mono(meth)acrylate, cyclopentoxy{polyethylene glycol-(poly)butylene glycol} mono(meth)acrylate, 15 cyclopentoxy{polyethylene glycol-(poly)propylene glycol-(poly)butylene glycol} mono(meth)acrylate, cyclohexoxypolyethylene glycol mono(meth)acrylate, cyclohexoxy{polyethylene glycol-(poly)propylene glycol} mono(meth)acrylate, cyclohexoxy{polyethylene glycol-(poly)butylene glycol} mono(meth)acrylate. 20 [0049]

25 As the aforementioned (alkoxy)polyalkylene glycol mono(meth)acrylate, in addition to the aforementioned compounds, it is preferable that phenoxypolyethylene glycol mono(meth)acrylate, phenoxy{polyethylene glycol (poly)(propyleneglycol)} mono(meth)acrylate, 30 phenoxy{polyethylene glycol (poly)butylene glycol} mono(meth)acrylate, phenoxy{polyethylene glycol (poly)propylene glycol (poly)butylene glycol} mono(meth)acrylate, (meth)allyloxypolyethylene glycol mono(meth)acrylate, (meth)allyloxy{polyethylene glycol (poly)propylene glycol} mono(meth)acrylate, 35



(meth)allyloxy(polyethylene glycol (poly)butylene glycol)  
mono(meth)acrylate, (meth)allyloxy(polyethylene glycol  
(poly)propylene glycol (poly)butylene glycol)  
mono(meth)acrylate.

5 [0050]

As the aforementioned polyalkylene glycol unsaturated  
monomer, in addition to the aforementioned monomers,  
(alkoxy)polyalkylene glycol monomaleic acid ester, and  
(alkoxy)polyalkylene glycol dimaleic acid ester are preferable.

10 As such a monomer, the followings are preferable.

Half esters and diesters derived from alkyl (poly)alkylene  
glycols obtained by addition of 1 to 500 moles of an oxyalkylene  
containing 2 to 18 carbon atoms to an alcohol containing 1 to  
30 carbon atoms or an amine containing 1 to 30 carbon atoms and  
15 the above-mentioned unsaturated dicarboxylic acid monomers;  
half esters and diesters derived from the above-mentioned  
unsaturated dicarboxylic acid monomers and polyalkylene glycols  
having an average number of moles of a glycol(s) containing 2  
to 18 carbon atoms as added of 2 to 500; half amides of maleamic  
20 acid with polyalkylene glycols having an average number of moles  
of a glycol(s) containing 2 to 18 carbon atoms as added of 2  
to 500; (poly)alkylene glycol di(meth)acrylates such as  
triethylene glycol di(meth)acrylate, (poly)ethylene glycol  
di(meth)acrylate, polypropylene glycol di(meth)acrylate, and  
25 (poly)ethylene glycol-(poly)propylene glycol  
di(meth)acrylate; (poly)alkylene glycol dimaleates such as  
triethylene glycol dimaleate and polyethylene glycol dimaleate;  
and the like.

[0051]

30 The aforementioned unsaturated carboxylic acid monomer  
may be a monomer having a group capable of forming a carboanion  
with a polymerizable unsaturated group, preferably a compound  
represented by the following formula (3).

[0052]



[0053]

In the formula,  $\text{R}^6$ ,  $\text{R}^7$  and  $\text{R}^8$  may be the same or different, represent a hydrogen atom, a methyl group, or  $-(\text{CH}_2)_z\text{COOM}^2$ , and  $z$  represents a number of 0 to 2.  $-(\text{CH}_2)_z\text{COOM}^2$  may form an anhydride with  $-\text{COOM}^1$  or other  $-(\text{CH}_2)_z\text{COOM}^2$ .  $\text{M}^1$  and  $\text{M}^2$  may be the same or different, and represent a hydrogen atom, a metal atom, an ammonium group or an organic amine group (organic ammonium group).

[0054]

As a metal atom in  $\text{M}^1$  and  $\text{M}^2$  in the formula (3), it is preferable that a monovalent metal atom such as an alkali metal atom, for example lithium, sodium and potassium; a divalent metal atom such as an alkaline earth metal atom, for example calcium and magnesium; a trivalent metal atom, for example aluminum and iron are preferable. As an organic amine group, an alkanolamine group such as an ethanolamine group, a diethanolamine group, and a triethanolamine group, and a triethylamine group are preferable. Further, the organic amine group may be an ammonium group.

[0055]

As the unsaturated carboxylic acid monomer, an unsaturated monocarboxylic acid monomer and an unsaturated dicarboxylic acid monomer are preferable. The unsaturated monocarboxylic acid monomer may be a monomer having each one of an unsaturated group and a group capable of forming a carboanion in a molecule. For example, acrylic acid, methacrylic acid, and crotonic acid; their monovalent metal salt, divalent metal salt, ammonium salt, and organic amine salt are preferable. Among them, from a viewpoint of improvement in cement dispersing performance, it is more preferable to use methacrylic acid; its monovalent metal salt,

divalent metal salt, ammonium salt, or organic amine salt.

The unsaturated dicarboxylic acid monomer may be a monomer having one unsaturated group and two groups capable of forming a carboanion in a molecule. Maleic acid, itaconic acid, citraconic acid, and fumaric acid, and their monovalent metal salt, divalent metal salt, ammonium salt and organic amine salt, and their anhydride are preferable.

[0056]

As the unsaturated carboxylic acid monomer, in addition to them, a half ester of an unsaturated dicarboxylic acid monomer and an alcohol having 1 to 22 carbon atom(s), a half amide of unsaturated dicarboxylic acids and amine having 1 to 22 carbon atom(s), a half ester of an unsaturated dicarboxylic acid monomer and glycol having 2 to 4 carbon atoms, and a half amide of maleamic acid and glycol having 2 to 4 carbon atoms may be also used.

[0057]

As a monomer copolymerizable with the aforementioned monomers, the following compounds can be used. (Meth)acrylic acid esters such as methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, butyl (meth)acrylate, pentyl (meth)acrylate, hexyl (meth)acrylate, decyl (meth)acrylate, and lauryl (meth)acrylate; difunctional (meth)acrylates such as hexanediol di(meth)acrylate; (meth)acrylate compounds such as hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate, methoxyethyl (meth)acrylate, ethoxyethyl (meth)acrylate, butoxyethylethyl (meth)acrylate, and methoxypropyl (meth)acrylate; amides of the aforementioned unsaturated monocarboxylic acid monomer and amine having 1 to 30 carbon atom(s), and unsaturated amides such as (meth)acrylamide, methyl(meth)acrylamide, (meth)acrylalkylamide, N-methylol(meth)acrylamide, and N,N-dimethyl(meth)acrylamide.

[0058]

Half esters and diesters derived from unsaturated dicarboxylic acid as mentioned above and alcohols containing

1 to 30 carbon atoms; half amides and diamides derived from the above-mentioned unsaturated dicarboxylic acid monomer and an amine containing 1 to 30 carbon atoms; half esters and diesters derived from the above-mentioned unsaturated dicarboxylic acid monomer and glycol containing 2 to 18 carbon atoms; half amide derived from maleamine acid and glycol containing 2 to 18 carbon atom; multifunctional (meth)acrylate such as hexanediol di(meth)acrylate, trimethylolpropane tri(meth)acrylate and trimethylolpropane di(meth)acrylate; unsaturated sulfonic acids and monovalent metal salt, divalent metal salt, ammonium salt and organic ammonium salt thereof, for example, vinylsulfonate, (meth)allylsulfonate, 2-(meth)acryloxyethylsulfonate, 3-(meth)acryloxypropylsulfonate, 3-(meth)acryloxy-2-hydroxypropylsulfonate, 3-(meth)acryloxy-2-hydroxypropyl sulfophenyl ether, 3-(meth)acryloxy-2-hydroxypropyloxysulfobenzoate, 4-(meth)acryloxybutylsulfonate, (meth)acrylamidomethylsulfonate, (meth)acrylamidoethylsulfonate, 2-methylpropanesulfonic acid (meth)acrylamide, and styrenesulfonic acid; vinyl aromatic compounds such as styrene,  $\alpha$ -methylstyrene, bromostyrene, chlorostyrene, vinyltoluene and p-methylstyrene;  $\alpha$ -olefins such as hexene, heptene and decene; alkyl vinyl ethers such as methyl vinyl ether, ethyl vinyl ether and butyl vinyl ether; allyl esters such as allyl acetate; allyls such as allyl alcohol; [0059]

alkanediol mono(meth)acrylates such as 1,4-butanediolmono(meth)acrylate, 1,5-pentanediol mono(meth)acrylate and 1,6-hexanediol mono(meth)acrylate; dienes such as butadiene, isoprene, isobutylene, 2-methyl-1,3-butadiene and 2-chloro-1,3-butadiene; unsaturated cyano compounds such as (meth)acrylonitrile and  $\alpha$ -chloroacrylonitrile; unsaturated esters such as vinyl acetate and vinyl propionate; unsaturated amines such as aminoethyl

(meth)acrylate, methylaminoethyl (meth)acrylate, dimethylaminoethyl (meth)acrylate, dimethylaminopropyl (meth)acrylate, dibutylaminoethyl (meth)acrylate and vinylpyridine; divinyl aromatics such as divinylbenzene; 5 cyanurates such as triallyl cyanurate; and siloxane derivatives such as polydimethylsiloxanepropylaminomaleamidic acid, polydimethylsiloxaneaminopropyleneaminomaleamidic acid, polydimethylsiloxane-bis(propylaminomaleamidic acid), polydimethylsiloxane-bis(dipropyleneaminomaleamidic acid), 10 polydimethylsiloxane-(1-propyl-3-acrylate), polydimethylsiloxane-(1-propyl-3-methacrylate), polydimethylsiloxane-bis(1-propyl-3-acrylate) and polydimethylsiloxane-bis(1-propyl-3-methacrylate). [0060]

15 As the aforementioned copolymerizable monomer, a polyalkyleneimine monomer having a polymerizable unsaturated group and an polyoxyalkylene group, and a monomer having a structure in which an oxyalkylene group is bound to a polyhydric alcohol residue may be also used, and examples include (1) a 20 macromer in which glycidyl methacrylate is added to a multi-branched polymer obtained by adding alkylene oxide to polyalkyleneimine, (2) a (meth)acrylic acid ester macromer of a multi-branched polymer in which alkylene oxide is added to polyalkyleneimine, and (3) a maleic acid ester macromer of a 25 multi-branched polymer in which alkylene oxide is added to polyalkyleneimine, that is, an ethylene monomer having a multi-branched polyoxyalkylene group of (1) to (3). As the multi-branched polymer, polyamidopolyamine or polyhydric alcohol to which alkylene oxide is added may be used. 30 [0061]

Examples of the polyalkyleneimine include a homopolymer and a copolymer obtained by polymerizing one or more kind(s) of alkyleneimines having 2 to 8 carbon atoms such as ethyleneimine, propyleneimine, 1,2-butyleneimine, 2,3-butyleneimine, and 35 1,1-dimethylethyleneimine by a conventional method. It is

preferable that they are formed using ethyleneimine as a main component. Such the polyalkyleneimine may be any of a straight structure, a branched structure, and a three-dimensionally crosslinked structure. Further examples may include

5 ethylenediamine, diethylenetriamine, triethylenetetramine, and tetraethylenepentamine. Such the polyalkyleneimine has usually a primary amino group or a secondary amino group (imino group) having an active hydrogen atom in addition to a tertiary amino group in a structure.

10 A weight average molecular weight of the polyalkyleneimine is preferably 100 to 1,000,000, more preferably 300 to 50,000, and still more preferably 600 to 10,000.

[0062]

As alkylene oxide to be added to the aforementioned  
 15 polyalkyleneimide, alkylene oxide having 2 to 8 carbon atoms such as ethylene oxide, propylene oxide, butylene oxide, isobutylene oxide, 1-butene oxide, 2-butene oxide, trimethylethylene oxide, tetramethylene oxide, tetramethylethylene oxide, butadiene monoxide, and octylene  
 20 oxide, and alicyclic epoxide such as dipentaneethylene oxide, and dihexaneethylene oxide; alicyclic epoxide such as trimethylene oxide, tetramethylene oxide, tetrahydrofuran, tetrahydropyran, and octylene oxide; aromatic epoxide such as styrene oxide, and 1,1-diphenylethylene oxide are preferable.  
 25 Among them, ethylene oxide, propylene oxide, and butylene oxide are preferable. Further, entity containing ethylene oxide as a main component is more preferable.

[0063]

In the alkylene oxide adduct, it is preferable that an  
 30 average molar number of addition of an oxyalkylene group is, for example, not smaller than 0.5 and not larger than 300. The molar number is more preferably 1 or more, and still more preferably 1.5 or more, particularly preferably 2 or more, most preferably 3 or more. In addition, the mole number is more preferably 200  
 35 or less, and still more preferably 150 or less, particularly

preferably 100 or less, most preferably 50 or less. When an average molar number of addition in an alkylene oxide adduct is outside such the range, there is a possibility that action and effect of a copolymer to make fluidity of a cement composition excellent are not sufficiently exerted.

[0064]

In the cement admixture of the present invention, when one or more kind(s) of polymers other than a polycarboxylic acid copolymer having a polyalkylene glycol side chain containing an essential oxyalkylene group having 3 or more carbon atoms may be contained, it is preferable that the polymer is obtained by polymerizing a monomer component containing a polyalkylene glycol unsaturated monomer in which an oxyalkylene group represented by  $-(R^aO)-$  in the formula (1) is all an oxyethylene group. Preferably, a monomer component contains an unsaturated carboxylic acid monomer and, if necessary, it may contain other copolymerizable monomer. Such the polyalkylene glycol unsaturated monomer, unsaturated carboxylic acid monomer and other copolymerizable monomer are the same as those as described above. In addition, a weight average molecular weight is the same as that of a copolymer in the embodiment of (1).

[0065]

As a process for preparing the cement admixture of the present invention, (i) a process of separately preparing two or more kinds of copolymers which are to constitute a polycarboxylic acid copolymer, and then mixing those copolymers, and (ii) a process of preparing two or more kinds of copolymers having different acid value, or having a weight average molecular weight of 20,000 or less in a series of polymerization steps by, for example, changing a ratio of monomers during polymerization are preferable. Preferable is a process of (i).

[0066]

As the production method of copolymer mentioned above, for example, any polymerization method can be used, such as water solution polymerization, polymerization in organic solvent,

emulsion polymerization or bulk polymerization using the monomer components and a polymerization initiator. For example, suitable as the above polymerization initiator, are persulfate salts such as ammonium persulfate, sodium persulfate and potassium persulfate; hydrogen peroxide; azo compounds such as azobis-2-methylpropionamidine hydrochloride and azoisobutyronitrile; peroxides such as benzoyl peroxide, lauroyl peroxide and cumene hydroperoxide; and so forth. Further, as the promoter, reducing agents such as sodium hydrogensulfite, sodium sulfite, Mohr's salt, sodium pyrodisulfite, formaldehyde sodium sulfoxylate, ascorbic acid and erythorbic acid; and amine compounds such as ethylenediamine, sodium ethylenediamine tetraacetate and glycine, etc. can be used in combination. These polymerization initiators and promoters may be used singly or two or more species may be used in combination.

[0067]

In the above method of copolymerization, a chain transfer agent may be used according to need. Usable as such chain transfer agent are one or two or more species of those known in the art.

Suitable as the hydrophobic chain transfer agent are thiol compounds having a hydrocarbon group containing not less than 3 carbon atoms or compounds whose solubility in water at 25°C is not more than 10%. For example, suitable are thiol chain transfer agents such as butanethiol, octanethiol, decanethiol, dodecanethiol, hexadecanethiol, octadecanethiol, cyclohexyl mercaptan, thiophenol, octyl thioglycolate, octyl 2-mercaptopropionate, octyl 3-mercaptopropionate, 2-ethylhexyl mercaptopropionate, 2-mercaptoethyl octanoate, 1,8-dimercapto-3,6-dioxaoctane, decanetrithiol, and dodecyl mercaptan; halides such as carbon tetrachloride, carbon tetrabromide, methylene chloride, bromoform, and bromotrichloroethane; unsaturated hydrocarbon compounds such as  $\alpha$ -methylstyrene dimer,  $\alpha$ -terpinene,  $\gamma$ -terpinene, dipentene,



and terpinolene; and the like. These may be used one or two or more species may be used in combination.

Also suitable as hydrophilic chain transfer agents are thiol chain transfer agents such as mercaptoethanol, 5 thioglycerol, thioglycolic acid, mercaptopropionic acid, 2-mercaptopropionic acid, 3-mercaptopropionic acid, thiomalic acid, and 2-mercaptoethanesulfonic acid; primary alcohols such as 2-aminopropane-1-ol; secondary alcohols such as isopropanol; phosphorous acid, hypophosphorous acid and salts thereof (e.g. 10 sodium hypophosphite, potassium hypophosphite), sulfurous acid, hydrosulfurous acid, dithionous acid, metabisulfurous acid, and salts thereof (e.g. sodium sulfite, sodium hydrogen sulfite, sodium dithionite, sodium metabisulfite, potassium sulfite, potassium hydrogen sulfite, potassium dithionite, potassium 15 metabisulfite), and like lower oxides and salts thereof. These may be used one or two or more species.

[0068]

As for the method of adding the above chain transfer agent to the reaction vessel, such a continuous charging method as 20 dripping and divided charging can be applied. The chain transfer agent may be introduced singly into the reaction vessel, or it may be admixed in advance with the monomer or solvent.

The above method of polymerization may be carried out either batchwise or continuously. As the solvent which is used 25 where necessary in the step of polymerization, any of known ones may be used and suitable are water; alcohols such as methyl alcohol, ethyl alcohol and isopropyl alcohol; aromatic or aliphatic hydrocarbons such as benzene, toluene, xylene, cyclohexane and n-heptane; esters such as ethyl acetate; and ketones such as 30 acetone and methyl ethyl ketone. These may be used one or two or more species may be used in combination. Among them, one or two or more solvents selected from the group consisting of water and lower alcohols containing 1 to 4 carbon atoms are preferably used from the viewpoint of solubility of the monomer 35 and the obtained copolymer.

[0069]

As for the method of adding the monomer polymerization initiator, etc. to the reaction vessel in the above-mentioned method of polymerization, suitable are the method comprising  
5 charging the reaction vessel with all monomer and then adding the polymerization initiator thereto to conduct copolymerization; the method comprising charging the reaction vessel with some of monomer and then adding the polymerization initiator and residual monomer components thereto to conduct  
10 polymerization; and the method comprising charging the reaction vessel with the polymerization solvent and then adding the whole amount of the monomers and polymerization initiator thereto are suitable. Among such methods, the method comprising carrying out the polymerization by adding dropwise the polymerization  
15 initiator and monomers successively to the reaction vessel is preferred since the molecular weight distribution of the product copolymer can be made narrow (sharp) and the cement dispersibility for increasing the fluidity of cement compositions and the like can be improved thereby. Furthermore,  
20 the copolymerization reaction is preferably carried out with maintaining the density of solvent in the reaction vessel during the polymerization to not more than 50% since the preservation stability of the obtained polymer is more improved by the improvement of the copolymerizability of the monomer components.  
25 More preferably, it is not more than 40%, still more preferably not more than 30%.

[0070]

In the above method of polymerization, the polymerization temperature and other polymerization conditions are  
30 appropriately selected according to the polymerization method, solvent, polymerization initiator, and chain transfer agent employed. It is generally preferred that the polymerization temperature be not lower than 0°C and not higher than 150°C. More preferably, 40 to 120°C, still more preferably 50 to 100°C,  
35 especially preferably 60 to 85°C.

[0071]

The polymer obtained by the above method of copolymerization as such can be used as the main component of cement admixtures. Where necessary, it may be used after further  
5 neutralization with an alkaline substance. Preferably used as the alkaline substance are inorganic salts such as monovalent and divalent metal hydroxides, chlorides and carbonates; ammonia; and organic amines, etc.

[0072]

10 The cement admixture of the present invention may contain, as an anti-foaming agent, a polyoxyalkylene compound containing at least one nitrogen atom and, at the same time, having an oxyethylene group and an oxyalkylene group having 3 or more carbon atoms in a molecule, and containing an aliphatic hydrocarbon  
15 structure in which 5 or more carbon atoms are bound successively. A cement admixture containing such the anti-foaming agent is also one of preferable embodiments of the present invention. One or more kind(s) of such the anti-foaming agents can be used.

[0073]

20 The polyoxyalkylene compound may be used by neutralizing a nitrogen atom with an inorganic acid such as hydrochloric acid, sulfuric acid and nitric acid, or an acidic substance such as acetic acid, propionic acid and (meth)acrylic acid. By blending such the polyoxyalkylene compound with the cement admixture of  
25 the present invention, water-solubility of a copolymer in the cement admixture is improved, and storage stability of an aqueous medium solution of a blend of an polyoxyalkylene compound and a copolymer becomes much better.

[0074]

30 It is preferable that the aforementioned oxyethylene group and an oxyalkylene group having 3 or more carbon atoms are present in a polyoxyalkylene compound as a polyoxyalkylene group in the added state and, when a polyoxyalkylene compound has a plurality of polyoxyalkylene groups, these may be the same or different.

35 A carbon number of an oxyalkylene group having 3 or more

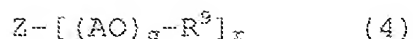
carbon atoms is preferably 8 or less, more preferably 6 or less, and still more preferably 4 or less. In addition, an addition form of an oxyalkylene group in a form in which two or more kinds of alkylene oxides, that is, ethylene oxide, and alkylene oxide  
5 having 3 or more carbon atoms are added, may be any of random addition, block addition and alternate addition. A preferable form is such that oxyethylene group-oxyalkylene group having 3 or more carbon atoms is added in a block manner.

[0075]

10 The aforementioned polyoxyalkylene compound has at least one aliphatic hydrocarbon structure in which 5 or more carbon atoms are bound successively. Examples of the aliphatic hydrocarbon structure in which 5 or more carbon atoms are bound successively, include an aliphatic hydrocarbon group having a  
15 structure in which 5 or more carbon atoms are bound successively, and an oxyalkylene group having a structure in which 5 or more carbon atoms are bound successively and, as long as such the structure is present in a molecule, the structure is not particularly limited. For example, an aliphatic hydrocarbon  
20 structure in which 5 or more carbon atoms are successively bound in an oxyalkylene group having 3 or more carbon atoms may be contained, or alternatively, an aliphatic hydrocarbon structure in which 5 or more carbon atoms are successively bound in a terminal hydrocarbon may be contained. In addition, as such the aliphatic  
25 hydrocarbon structure, it is preferable that a structure in which 8 or more, more preferably 10 or more, and still more preferably more than 12 carbon atoms are bound successive. When a polyoxyalkylene compound having an aliphatic hydrocarbon structure having 12 or more carbon atoms is used, quality of  
30 the air in a concrete composition can be made to be better. In addition, 30 or less carbon atoms are preferable. 22 or less is more preferable.

[0076]

35 It is preferable to use, as the polyoxyalkylene compound, a compound represented by the following formula (4):



(wherein Z represents a compound residue having active hydrogen, R<sup>9</sup>s are the same or different, and represent a hydrogen atom, a hydrocarbon group, -Y-NR<sup>10</sup>R<sup>11</sup>, -COR<sup>12</sup> or -CH<sub>2</sub>CH<sub>2</sub>NHCO-R<sup>13</sup>, Y represents an alkylene group having 1 to 10 carbon atom(s), R<sup>10</sup> and R<sup>11</sup> are the same or different, and represent a hydrogen atom or a hydrocarbon group having 1 to 30 carbon atom(s), R<sup>12</sup> and R<sup>13</sup> represent a hydrocarbon group having 1 to 30 carbon atom(s), or a group having at least one carboxyl group or sulfonyl group or a salt thereof, AOs are the same or different, and represent an oxyalkylene group having 2 to 18 carbon atoms, "q"s are the same or different, and represent an average molar number of addition of an oxyalkylene group, and is 1 to 300, r is 1 to 300 and, regarding the total molar number of addition of the oxyethylene group in the oxyalkylene group as u and a total molar number of addition of an oxyalkylene group having 3 or more carbon atoms to be v, a relationship of 0.1 < u / (u+v) < 0.9, 1 < u+v < 300 is satisfied). In addition, in a polyoxyalkylene compound, represented by the formula (4), a group represented by Z and/or a group represented by R<sup>9</sup> has a nitrogen atom.

[0077]

In the formula (4), Z represents a compound residue having active hydrogen. A compound residue having active hydrogen means a group having a structure obtained by removing active hydrogen from a compound having active hydrogen, and is not particularly limited to a group which is formed by a reaction with a compound having active hydrogen. In addition, in a polyoxyalkylene compound, a compound residue having active hydrogen may be one or more kind(s). As such the group, a residue of an alcohol having a structure in which active hydrogen is removed from a hydroxyl group of an alcohol, a residue of carboxylic acid having a structure in which active hydrogen is removed from a carboxyl group of carboxylic acid, a residue of amine having a structure in which active hydrogen is removed from an amino group of amine, a residue of imine having a structure

in which active hydrogen is removed from an imino group of imine, and a residue having a structure in which active hydrogen is removed from a thiol group of thiol are preferable. Among them, a residue of alcohol, and a residue of amine or imine are preferable.  
 5 A form of a compound residue having active hydrogen may be any of chain-like, branched, and three-dimensionally crosslinked structures.

Regarding a preferable embodiment of the aforementioned compound residue having active hydrogen, as a residue of alcohol,  
 10 a residue having a structure in which active hydrogen is removed from a monohydric alcohol or a polyhydric alcohol such as trimethylolpropane, pentaerythritol, polyglycerin and sorbitol is preferable, as a residue of amine, a residue having a structure in which active hydrogen is removed from monovalent amine or  
 15 polyvalent amine is preferable and, as a residue of imine, a residue having a structure in which active hydrogen is removed from diethyleneimine or polyethyleneimine is preferable.  
 [0078]

In the formula (4),  $R^9$ s are the same or different, and  
 20 represent a hydrogen atom, a hydrocarbon group,  $-Y-NR^{10}R^{11}$ ,  $-COR^{12}$  or  $-CH_2CH_2NHCO-R^{13}$ . As a hydrocarbon group, a straight or branched alkyl group having 1 to 30 carbon atom(s); an aromatic group having a benzene ring which have 6 to 30 carbon atoms such as a phenyl group, an alkyl phenyl group, a phenyl alkyl group,  
 25 a phenyl group substituted with an (alkyl)phenyl group, and a naphthyl group; an alkenyl group having 2 to 30 carbon atoms; an alkynyl group having 2 to 30 carbon atoms are preferable. In addition, a carbon number of a hydrocarbon group has 1 or more carbon atom(s), and in order that a polyoxyalkylene compound  
 30 has high anti-foaming performance, a carbon number is preferably 2 or more, more preferably 5 or more, and still more preferably more than 12. In addition, a carbon number is preferably 30 or less, more preferably 22 or less, and still more preferably 18 or less. Moreover, among hydrocarbon groups, a straight or  
 35 branched alkyl group, and alkenyl group are particularly

preferable.

[0079]

The Y represents an alkylene group having 1 to 10 carbon atom(s), and a carbon number is preferably 2 or more, and preferably 8 or less. The  $R^{10}$  and  $R^{11}$  represent a hydrogen atom or a hydrocarbon group having 1 to 30 carbon atom(s) and, when there is no aliphatic hydrocarbon structure in which 5 or more carbon atoms are bound to Z or AO in the formula (4), a carbon number of a hydrocarbon group in  $R^{10}$  and  $R^{11}$  is preferably 5 or more, more preferably 8 or more, and still more preferably 10 or more. In addition, a carbon number is and still more preferably more than 12. In addition, a carbon number is preferably 22 or less. Conversely, when there is an aliphatic hydrocarbon structure in which 5 or more carbon atoms are successively bound to Z or AO,  $R^{10}$  and  $R^{11}$  are preferably a hydrogen atom.  $R^{12}$  and  $R^{13}$  represent a hydrocarbon group having 1 to 30 carbon atom(s), or a group having at least one carboxyl group or sulfonyl group or a salt thereof and, when there is no aliphatic hydrocarbon structure in which 5 or more carbon atoms are successively bound to Z or AO in the formula (4), a hydrocarbon group having 5 or more carbon atoms is preferable. In contrast, when there is an aliphatic hydrocarbon structure in which 5 or more carbon atoms are successively bound to Z or AO, a group having at least one carboxyl group or sulfonyl group or a salt thereof is preferable. Among hydrocarbon groups, a straight or branched alkyl group, and alkenyl group are particularly preferable.

[0080]

The AO represents an oxyalkylene group having 2 to 18 carbon atoms, and a carbon number is preferably 8 or less, more preferably 6 or less, and still more preferably 4 or less. An addition embodiment of an oxyethylene group and an oxyalkylene group having 3 or more carbon atoms may be any of random manner, block manner and alternate manner. A more preferable embodiment is block manner. In addition, the u and v represent a total molar

number of addition of an oxyethylene group and a total molar number of addition of an oxyalkylene group having 3 or more carbon atoms, respectively, and it is preferable to satisfy a relationship of  $0.1 < u/(u+v) < 0.9$ ,  $1 < u+v < 300$ .  $(u+v)$  is more preferably more than 5, and still more preferably more than 10. In addition,  $(u+v)$  is preferably less than 200, more preferably less than 150, and still more preferably less than 100, particularly preferably less than 80, most preferably less than 50. In the formula (4), an average molar number of addition  $q$  means an average value of a mole number of an oxyalkylene group which is added per 1 mole of the same unit among units represented by  $[(AO)_q-R^9]$ .

[0081]

In addition, it is preferable that  $u/(u+v)$  which is a ratio of a total molar number of addition  $u$  of an oxyethylene group relative to a total molar number of addition  $(u+v)$  of alkylene oxide satisfies a relationship of  $0.1 < u/(u+v) < 0.9$ . When the ratio is 0.9 or more, there is a possibility that hydrophilicity becomes too strong, and anti-foaming property becomes not sufficient in some cases. When the ratio is 0.1 or less, there is a possibility that anti-foaming property can not be endured. In either case, a strength of a hardening product is reduced. A value of  $u/(u+v)$  is more preferably more than 0.15, and still more preferably more than 0.2, particularly preferably more than 0.3. In addition, the value is more preferably less than 0.8, and still more preferably less than 0.7, particularly preferably less than 0.55, most preferably less than 0.5.

[0082]

In addition, it is preferable that  $(u+v)$  satisfies a relationship of  $1 < u+v < 300$ .  $(u+v)$  is more preferably more than 5, and still more preferably more than 10. In addition,  $(u+v)$  is preferably less than 200, more preferably less than 150, and still more preferably less than 100, particularly preferably less than 80, most preferably less than 50.



[0083]

The  $r$  is 1 to 300, and is preferably 200 or less, more preferably 100 or less. When  $r$  is 2 or more, that is, when a plurality of groups represented by  $-(\text{AO})_q-\text{R}^9$  are bound to Z, groups represented by  $-(\text{AO})_q-\text{R}^9$  may be the same or different.

[0084]

Since a polyoxyalkylene compound in the formula (4) has at least one aliphatic hydrocarbon structure in which 5 or more carbon atoms are successively bound in a molecule, there is, in the formula (4), an aliphatic hydrocarbon structure in which 5 or more successive carbon atoms are bound, in at least one of structures represented by  $\text{R}^9$ , Z,  $\text{R}^9-\text{AO}$  and AO constituting a polyoxyalkylene compound. As such the aliphatic hydrocarbon structure, a structure in which 10 or more hydrocarbon atoms are bound successively, is preferable. In addition, 30 or less is preferable. 22 or less is more preferable.

[0085]

A molecular weight of a polyoxyalkylene compound in the present invention is preferably 10,000 or less, more preferably 5,000 or less, and preferably 100 or more, more preferably 200 or more.

[0086]

As a compound represented by the formula (4), a primary amine having a straight or branched alkyl group having 1 to 30 carbon atom(s) such as (di)methylamine, (di)ethylamine, (di)propylamine, (di)butylamine, (di)pentylamine, (di)hexylamine, (di)heptylamine, (di)octylamine, (di)nonylamine, (di)decaamine, (di)undecaamine, (di)dodecaamine, (di)tetradecaamine, (di)pentadecaamine, (di)hexadecaamine, (di)heptadecaamine, (di)octadecaamine, (di)nonadecaamine, and (di)icosaamine; a secondary amine having the same kinds of alkyl groups or different kinds of alkyl groups; a primary amine having a straight or branched alkyl group having 1 to 30 carbon atom(s) such as a primary amine derived from fatty acid obtained from a palm oil, a primary amine derived from oleic

acid, a primary amine derived from fatty acid obtained from a soybean oil, a primary amine derived from fatty acid obtained from beef tallow; and a primary amine derived from fatty acid obtained from hardened tallow and in which a different kind of an alkyl group is mixed; a secondary amine having a straight or branched alkyl group having 1 to 30 carbon atom(s) such as a secondary amine derived from fatty acid obtained from a palm oil, a secondary amine derived from oleic acid, a secondary amine derived from fatty acid obtained from a soybean oil, a secondary amine derived from fatty acid obtained from beef tallow, and a secondary amine derived from fatty acid obtained from hardened tallow and in which a different kind of an alkyl group is mixed; a primary or secondary amine having an aromatic group having a benzene ring and having 6 to 30 carbon atoms such as an aromatic group having a phenyl group, an alkylphenyl group, a phenylalkyl group, a phenyl group substituted with an (alkyl)phenyl group, and a naphthyl group, an alkenyl group having 2 to 30 carbon atoms, or an alkynyl group having 2 to 30 carbon atoms; an adduct obtained by adding ethylene oxide and alkylene oxide having 3 to 18 carbon atoms to amines such as alkanol amines such as monoethanolamine, diethanolamine, and triethanolamine are preferable.

[0087]

In addition, as a compound having two or more nitrogen atoms among the compounds represented by the formula (4), ethylene oxide adducts and alkylene oxide adducts having 3 to 18 carbon atoms of amidoamines obtained by dehydration-condensing polyalkylene polyamines such as ethylenediamine, propylenediamine, diethylenetriamine, triethylenetetramine, dipropylenetriamine, and tetrapropylenepentamine, and fatty acids such as acetic acid, propionic acid, butyric acid, valeric acid, lauric acid, stearic acid, oleic acid, fatty acid obtained from a palm oil, fatty acid obtained from a soybean oil, fatty acid obtained from beef tallow, and fatty acid obtained from hardened tallow; ethylene

oxide adducts and alkylene oxide adducts having 3 to 18 carbon atoms of imidazolines obtained by dehydration-condensing polyalkylenepolyamines such as ethylenediamine, propylenediamine, diethylenetriamine, triethylenetetramine, 5 dipropylenetriamine, and tetrapropylenepentamine, and fatty acids such as acetic acid, propionic acid, butyric acid, valeric acid, lauric acid, stearic acid, oleic acid, fatty acid obtained from a palm oil, fatty acid obtained from a soybean oil, fatty acid obtained from beef tallow, and fatty acid obtained from 10 hardened tallow to obtain amidoamines, and further dehydrated to obtained amidoamines; ethylene oxide adducts and alkylene oxide adducts having 3 to 18 carbon atoms of polyalkylenepolyamines such as ethylenediamine, propylenediamine, diethylenetriamine, triethylenetetramine, 15 dipropylenetriamine, and tetrapropylenepentamine; ethylene oxide adducts and alkylene oxide adducts having 3 to 18 carbon atoms of polyalkylenepolyamines such as ethylenediamine, propylenediamine, diethylenetriamine, triethylenetetramine, dipropylenetriamine, and tetrapropylenepentamine which are 20 modified with a hydrocarbon group having 1 to 30 carbon atom(s); ethylene oxide adducts and alkylene oxide adducts having 3 to 18 carbon atoms of polyalkyleneimines such as polyethyleneimine, and polypropyleneimine obtained by polymerizing alkyleneimine such as ethyleneimine, propyleneimine; ethylene oxide and 25 alkylene oxide having 3 to 18 carbon atoms adducts of polyalkyleneimines such as polyethyleneimine, and polypropyleneimine obtained by polymerizing alkyleneimine such as ethyleneimine, and propyleneimine which are modified with a hydrocarbon group having 1 to 30 carbon atom(s); ethylene oxide 30 and alkylene oxide having 3 to 18 carbon atoms adducts of alkylaminopropylamines obtained by adding acrylonitrile to primary amine or secondary amine having a hydrocarbon group having 1 to 30 carbon atom(s), and then reducing the adduct, are preferable.

35 [0088]

As a nitrogen atom-containing polyoxyalkylene compound, the following compounds are also preferable.

Amines obtained by adding ethylene oxide and alkylene oxide having 3 to 18 carbon atoms to monohydric alcohols having a hydrocarbon group having 1 to 30 carbon atom(s) to obtain polyoxyalkylenes, and introducing an amino group therein; amines obtained by introducing an amino group into polyoxyethylene polyoxyalkylene having hydroxyl groups at both ends; amines obtained by adding ethylene oxide and alkylene oxide having 3 to 18 carbon atoms to a polyhydric alcohol having 3 or more hydroxyl groups in a molecule to obtain polyoxyalkylenes, and introducing an amino group therein; amines obtained by adding ethylene oxide and alkylene oxide having 3 to 18 carbon atoms to alcohols having an acetylene group in a molecule to obtain polyoxyalkylenes, and introducing an amino group therein.

There are contemplated a variety of methods of introducing an amino group, but a method of converting a hydroxy group itself into an amino group with various amination reagents, and a method of adding alkyleneimine such as ethyleneimine and propyleneimine to a hydroxy group are preferable.

[0089]

As a monohydric alcohol having a hydrocarbon group having 1 to 30 carbon atom(s), a straight or branched saturated alcohol such as methanol, ethanol, propanol, isopropanol, butanol, pentanol, hexanol, octanol, lauryl alcohol, cetyl alcohol, stearyl alcohol, a straight or branched alcohol having 12 to 14 carbon atoms; an unsaturated alcohol such as allyl alcohol, methallyl alcohol, 3-methyl-3-buten -1-ol, 3-methyl-2-buten -1-ol, 2-methyl-3-buten -2-ol, oleyl alcohol; an aromatic alcohol such as phenol, nonyl phenol, benzyl alcohol are preferable.

[0090]

As polyoxyethylene polyoxyalkylenes having a hydroxy group on both ends, AB type block type such as polyoxyethylene polyoxypropylene, and polyoxyethylene polyoxybutylene; ABA

block type such as polyoxyethylene polyoxypropylene polyoxyethylene, polyoxypropylene polyoxyethylene polyoxypropylene, and polyoxyethylene polyoxybutylene polyoxyethylene are preferable.

5 [0091]

As the polyhydric alcohol having 3 or more hydroxyl groups in a molecule, trimethylolpropane, pentaerythritol, polyglycerin and sorbitol are preferable.

[0092]

10 As the alcohols having an acetylene group in a molecule, 2,4,7,9-tetramethyl-5-decyn-4,7-diol, 2,5-dimethyl-3-hexyn-2,5-diol, and 3-methyl-1-butyn-3-ol are preferable.

[0093]

15 When no aliphatic hydrocarbon structure in which 5 or more carbon atoms are successively bound in a molecule is contained in the aforementioned polyoxyalkylene compound, an aliphatic hydrocarbon structure may be appropriately introduced by partially adding alkylene oxide having 5 to more carbon atoms, 20 or reacting with alkyl halide having 5 to more carbon atoms during synthesis or after synthesis.

[0094]

In addition, a compound obtained by further adding alkylene oxides such as ethylene oxide or alkyleneimines such as 25 ethyleneimine to a terminal functional group of the aforementioned polyoxyalkylene compound may be also used as a polyoxyalkylene compound.

[0095]

30 Further, a compound obtained by reacting a terminal functional group of the aforementioned polyoxyalkylene compound with an acid anhydride such as acetic anhydride and butyric anhydride may be also used as a polyoxyalkylene compound in the present invention.

[0096]

35 In addition, as a polyoxyalkylene compound, the following

compounds are also preferable.

Compounds obtained by esterification-binding the  
aforementioned polyoxyalkylene compound and a compound having  
two or more carboxyl groups while leaving at least one carboxyl  
5 group; compounds obtained by esterification-binding the  
aforementioned polyoxyalkylene compound and a compound having  
a carboxyl group and a sulfonyl group while leaving at least  
one sulfonyl group; compounds obtained by amido-binding the  
aforementioned polyoxyalkylene compound and a compound having  
10 two or more carboxyl groups while leaving at least one carboxyl  
group; compounds obtained by amido-binding the aforementioned  
polyoxyalkylene compound and a compound having a carboxyl group  
and a sulfonyl group while leaving at least one sulfonyl group.

In such the polyoxyalkylene compound, a remaining carboxyl  
15 group or sulfonyl group may be various metal salts such as a  
sodium salt and a calcium salt which are neutralized with a base  
such as sodium hydroxide and calcium hydroxide, an ammonium salt,  
or an amine salt.

[0097]

20 As the aforementioned compound having two or more carboxyl  
groups, unsaturated dicarboxylic acids such as maleic acid,  
fumaric acid, phthalic acid and itaconic acid, and a metal salt,  
an ammonium salt, an amine salt thereof; saturated dicarboxylic  
acids such as succinic acid, malonic acid, glutaric acid and  
25 adipic acid, and a metal salt, an ammonium salt, and an amine  
salt thereof; a low-molecular polymer of unsaturated  
monocarboxylic acid or unsaturated dicarboxylic acid such as  
an acrylic acid oligomer, a methacrylic acid oligomer and a maleic  
acid oligomer, and a metal salt, an ammonium salt and an amine  
30 salt thereof are preferable.

[0098]

The aforementioned polyoxyalkylene compound can be  
obtained, for example, by reacting a polyoxyalkylene compound  
having a hydroxy group at an end and acid anhydride such as maleic  
35 anhydride and succinic anhydride without a solvent or in a

suitable solvent. Thereupon, it is preferable to use a suitable base catalyst. Alternatively, the polyoxyalkylene compound can be also obtained by esterification by dehydration-reacting a polyoxyalkylene compound having a hydroxy group at an end and  
5 carboxylic acid, or a transesterification reaction of a polyoxyalkylene compound having a hydroxy group at an end and an ester compound.

[0099]

In the present invention, among the polyoxyalkylene  
10 compounds represented by the formula (4), when  $R^3$  is a hydrogen atom, or when Z has -OH or -NH<sub>2</sub>, an unsaturated monomer having anti-foaming property can be synthesized by esterification and amidation with unsaturated carboxylic acid such as (meth)acrylic acid and maleic acid. By copolymerizing this unsaturated  
15 monomer having anti-foaming property with the aforementioned monomer component, an anti-foaming component can be incorporated into a polymer skeleton. A cement admixture containing a polymer in which such the anti-foaming component is incorporated into the cement admixture of the present invention is also one of  
20 embodiments of the present invention.

[0100]

When the cement admixture of the present invention containing the aforementioned polyoxyalkylene compound is used in a cement composition, a ratio of a polyoxyalkylene compound  
25 to be blended is preferably 0.0001% by weight or more, and preferably 1.0% by weight or less of cement weight. When the blending ratio is smaller than 0.0001% by weight, there is a possibility that performance is insufficient. Even when an amount exceeding 1.0% by weight is used, there is a possibility  
30 that the effect becomes substantially plateau, and this is also disadvantageous from economical point of view. The blending ratio is more preferably 0.0005% by weight or more, and still more preferably 0.001% by weight or more. And, the blending ratio is preferably 0.5% by weight or less, and still more  
35 preferably 0.1% by weight or less. An amount corresponding to

such the ratio may be added. By this addition, various preferable effects such as reduction in a unit water amount, increase in a strength, and improvement in durability are exerted.

[0101]

5       The cement admixture of the present invention is preferably in a form of an aqueous solution from a viewpoint of handling. In addition, the cement admixture of the present invention may contain other additive, or when the cement admixture of the present invention is mixed with cement, other additive may be added. As the other additive, the known cement additives may be used. For example, one or more kind(s) of the following additives can be used.

[0102]

(1) Water-soluble macromolecular substances; unsaturated  
15   carboxylic acid polymers such as polyacrylic acid (sodium salt), polymethacrylic acid (sodium salt), polymaleic acid (sodium salt) and acrylic acid-maleic acid copolymer sodium salt; polyoxyethylene or polyoxypropylene polymers or copolymers thereof, such as polyethylene glycol and polypropylene glycol;  
20   nonionic cellulose ethers such as methylcellulose, ethylcellulose, hydroxymethylcellulose, hydroxyethylcellulose, carboxymethylcellulose, carboxyethylcellulose and hydroxypropylcellulose; polysaccharides produced by microbial fermentation, such as  
25   yeast glucans, xanthan gum,  $\beta$ -1,3-glucans (which may be straight chained or branched; e.g. curdlan, paramylum, pachyman, scleroglucan, laminaran); polyacrylamide; polyvinyl alcohol; starch; starch phosphate; sodium alginate; gelatin; amino-containing acrylic acid copolymers and quaternization  
30   products derived therefrom; and the like;

[0103]

(2) Polymer emulsions; copolymers of various vinyl monomers such as alkyl (meth)acrylates; and the like;  
(3) Retarders; oxycarboxylic acids (or salts thereof) and  
35   inorganic or organic salts, such as gluconic acid, glucoheptonic



- acid, arabonic acid, malic acid and citric acid, and sodium, potassium, calcium, magnesium, ammonium and triethanolamine salts thereof; saccharides, for example monosaccharides, disaccharides, trisaccharides and like oligosaccharides, such as glucose, fructose, galactose, saccharose, xylose, apiose, ribose and isomerized saccharide, oligosaccharides such as dextrin, polysaccharides such as dextran, molasses and like mixtures containing these; sugar alcohols such as sorbitol; magnesium fluorosilicate; phosphoric acid and salts thereof or borate esters; aminocarboxylic acids and salts thereof; alkali-soluble proteins; humic acid; tannic acid; phenols; polyhydric alcohols such as glycerol; phosphonic acids and derivatives thereof, such as aminotri (methylenephosphonic acid), 1-hydroxyethylidene-1,1-diphosphonic acid, ethylenediaminetetra (methylenephosphonic acid), diethylenetriaminepenta (methylenephosphonic acid) and alkali metal salts and alkaline earth metal salts of these; and the like;
- [0104]
- (4) High-early-strength agents or accelerators; soluble calcium salts such as calcium chloride, calcium nitrite, calcium nitrate, calcium bromide and calcium iodide; chlorides such as iron chloride and magnesium chloride; sulfate salts; potassium hydroxide; sodium hydroxide; carbonate salts; thiosulfate salts; formic acid and formate salts such as calcium formate; alkanolamines; alumina cement; calcium aluminosilicate; and the like;
- (5) Mineral oil antifoaming agents; kerosene, liquid paraffin, etc.;
- (6) Fat or oil antifoaming agents; animal/vegetable oils, sesame oil, castor oil, alkylene oxide adducts derived from these, and the like;
- (7) Fatty acid antifoaming agents; oleic acid, stearic acid, alkylene oxide adducts derived from these, and the like;
- (8) Fatty acid ester antifoaming agents; glycerin

monoricinolate, alkenylsuccinic acid derivatives, sorbitol monolaurate, sorbitol trioleate, natural waxes, etc.;

[0105]

- (9) Oxyalkylene antifoaming agents; polyoxyalkylenes such as  
 5 (poly)oxyethylene-(poly)oxypropylene adducts; (poly)oxyalkyl ethers such as diethylene glycol heptyl ether, polyoxyethylene oleyl ether, polyoxypropylene butyl ether, polyoxyethylene-polyoxypropylene 2-ethylhexyl ether and oxyethylene-oxypropylene adducts of higher alcohols containing  
 10 12 to 14 carbon atoms; (poly)oxyalkylene (alkyl)aryl ethers such as polyoxypropylene phenyl ether and polyoxyethylene nonylphenyl ether; acetylene ethers derived from acetylene alcohol by addition polymerization of an alkylene oxide, such as 2,4,7,9-tetramethyl-5-decyne-4,7-diol,  
 15 2,5-dimethyl-3-hexyne-2,5-diol and 3-methyl-1-butyne-3-ol; (poly)oxyalkylene fatty acid esters such as diethylene glycol oleate, diethylene glycol laurate and ethylene glycol distearate; (poly)oxyalkylenesorbitan fatty acid esters such as polyoxyethylenesorbitan monolaurate and  
 20 polyoxyethylenesorbitan trioleate; (poly)oxyalkylene alkyl(aryl) ether sulfate ester salts such as sodium polyoxypropylenemethyl ether sulfate and sodium polyoxyethylene dodecylphenol ether sulfate; (poly)oxyalkylenealkyl phosphate esters such as  
 25 (poly)oxyethylenestearyl phosphate; (poly)oxyalkylenealkylamines such as polyoxyethylenelaurylamine; polyoxyalkyleneamides; etc.;

[0106]

- (10) Alcohol antifoaming agents; octyl alcohol, hexadecyl  
 30 alcohol, acetylene alcohol, glycols, etc.;
- (11) Amide antifoaming agents; acrylate polyamines etc.;
- (12) Phosphate ester antifoaming agents; tributyl phosphate, sodium octyl phosphate, etc.;
- (13) Metal soap antifoaming agents; aluminum stearate, calcium  
 35 oleate, etc.;

- (14) Silicone antifoaming agents; dimethylsilicone oils, silicone pastes, silicone emulsions, organic modified polysiloxanes (polyorganosiloxanes such as dimethylpolysiloxane), fluorosilicone oils, etc.;
- 5 (15) AE (air-entraining) agents; resin soaps, saturated or unsaturated fatty acids, sodium hydroxystearate, lauryl sulfate, ABS (alkylbenzenesulfonates), LAS (linear
- 10 alkylbenzenesulfonates), alkanesulfonates, polyoxyethylene alkyl(phenyl) ethers, polyoxyethylene alkyl(phenyl) ether sulfates and salts thereof, polyoxyethylene alkyl(phenyl) ether phosphates and salts thereof, proteinous materials, alkenylsulfosuccinic acids,  $\alpha$ -olefinsulfonates, etc.;
- [0107]
- (16) Other surfactants; polyalkylene oxide derivatives
- 15 produced by addition of not less than 10 moles of an alkylene oxide, such as ethylene oxide and/or propylene oxide to monohydric aliphatic alcohol containing 6 to 30 carbon atoms, such as octadecyl alcohol or stearyl alcohol, a monohydric alicyclic alcohol containing 6 to 30 carbon atoms, such as abietyl
- 20 alcohol, a monomercaptan containing 6 to 30 carbon atoms, such as dodecyl mercaptan, an alkylphenol containing 6 to 30 carbon atoms, such as nonylphenol, an amine containing 6 to 30 carbon atoms, such as dodecylamine, or a carboxylic acid containing 6 to 30 carbon atoms, such as lauric acid or stearic acid; alkyl
- 25 diphenyl ether sulfonate salts containing two sulfo-containing phenyl groups, which may have an alkyl or alkoxy group as a substituent, bound together by ether bonding; various anionic surfactants, various cationic surfactants such as alkylamine acetates and alkyltrimethylammonium chlorides; various
- 30 nonionic surfactants; various amphoteric surfactants; and the like;
- [0108]
- (17) Water-proof agents; fatty acids (salts), fatty acid esters, fats and oils, silicones, paraffins, asphalts, waxes, etc.;
- 35 (18) Corrosion inhibitors; nitrite salts, phosphate salts,

zinc oxide, etc.;

(19) Crack inhibitors; polyoxyalkyl ethers; alkanediols such as 2-methyl-2,4-pentanediol; etc.;

(20) Expansive additives; ettringite materials, coals, etc.

5 [0109]

As other known cement additives (admixtures), These can be used that cement wetting agents, thickening agents, segregation reducing agents, flocculants, drying shrinkage reducing agents, agents to increase strength, self-leveling agents, corrosion inhibitors, color difference agents, antifungal agents, blast-furnace slag, fly ash, cinder ash, clinker ash, husk ash, silica fume, silica powder, gypsum and so forth.

[0110]

15 Furthermore, the cement admixture of the present invention can be used in combinations with any of those cement dispersants which are well known in the art. For example, as one or two or more species in the following can be used.

ligninsulfonates; polyol derivatives;  
 20 naphthalenesulfonic acid-formaline condensates;  
 melaminesulfonic acid-formaline condensates;  
 polystyrenesulfonic acid salts; aminosulfonic acid compounds such as aminoarylsulfonic acid-phenol-formaldehyde condensates as described in Japanese Kokai Publication Hei-01-113419; cement  
 25 dispersants comprising, as component (a), a copolymer of a polyalkylene glycol mono(meth)acrylate compound and a (meth)acrylic acid compound and/or a salt of said copolymer, as component (b), a copolymer of a polyalkylene glycol mono(meth)allyl ether compound and maleic anhydride and/or a  
 30 hydrolyzate of said copolymer and/or a salt thereof and, as component (c), a copolymer of a polyalkylene glycol mono(meth)allyl ether compound and a maleic acid ester of a polyalkyleneglycol compound, and/or a salt thereof, as described in Japanese Kokai Publication Hei-07-267705; concrete  
 35 admixtures comprising, as component A, a copolymer of a

polyalkylene glycol (meth)acrylate and (meth)acrylic acid (or a salt thereof), as component B, a specific polyethylene glycol-polypropylene glycol compound and, as component C, a specific surfactant, as described in JP 2508113; copolymers of

5 polyethylene(propylene) glycol (meth)acrylate or polyethylene(propylene) glycol mono(meth)allyl ether, (meth)allylsulfonic acid (or a salt thereof) and (meth)acrylic acid (or a salt thereof), as described in Japanese Kokai Publication Sho-62-216950;

10 [0111]

copolymers of polyethylene(propylene) glycol (meth)acrylate, (meth)allylsulfonic acid (or a salt thereof) and (meth)acrylic acid (or a salt thereof), as described in Japanese Kokai Publication Hei-01-226757; copolymers of

15 polyethylene(propylene) glycol (meth)acrylate, (meth)allylsulfonic acid (or a salt thereof) or p-(meth)allyloxybenzenesulfonic acid (or a salt thereof) and (meth)acrylic acid (or a salt thereof), as described in Japanese Kokoku Publication Hei-05-36377; copolymers of polyethylene

20 glycol mono(meth)allyl ether and maleic acid (or a salt thereof), as described in Japanese Kokai Publication Hei-04-149056; copolymers of polyethylene glycol (meth)acrylate, (meth)allylsulfonic acid (or a salt thereof), (meth)acrylic acid (or a salt thereof), an alkanediol mono(meth)acrylate, a

25 polyalkylene glycol mono(meth)acrylate and an  $\alpha, \beta$ -unsaturated monomer having an amide group within the molecule, as described in Japanese Kokai Publication Hei-05-170501; copolymers of polyethylene glycol mono(meth)allyl ether, polyethylene glycol mono(meth)acrylate, an alkyl (meth)acrylate, (meth)acrylic

30 acid (or a salt thereof) and (meth)allylsulfonic acid (or a salt thereof) or p-(meth)allyloxybenzenesulfonic acid (or a salt thereof), as described in Japanese Kokai Publication Hei-06-191918; copolymers of an alkoxypolyalkylene glycol monoallyl ether and maleic anhydride, or hydrolyzates thereof,

35 or salts thereof, as described in Japanese Kokai Publication

Hei-05-43288; copolymers of polyethylene glycol monoallyl ether, maleic acid and a monomer copolymerizable with these monomers, or salts thereof, or esters thereof, as described in Japanese Kokoku Publication Sho-58-38380;

5 [0112]

copolymers of a polyalkylene glycol mono(meth)acrylate monomer, a (meth)acrylic acid monomer and a monomer copolymerizable with these monomers, as described in Japanese Kokoku Publication Sho-59-18338; copolymers of a (meth)acrylic acid ester having a sulfonic acid group and a monomer copolymerizable with these as necessary, or salts thereof, as described in Japanese Kokai Publication Sho-62-119147; esterification reaction products from a copolymer of an alkoxypolyalkylene glycol monoallyl ether and maleic anhydride and an alkenyl-terminated polyoxyalkylene derivative, as described in Japanese Kokai Publication Hei-06-271347; esterification reaction products from a copolymer of an alkoxypolyalkylene glycol monoallyl ether and maleic anhydride and a hydroxy-terminated polyoxyalkylene derivative, as described in Japanese Kokai Publication Hei-06-298555; copolymers of alkenyl ether monomer obtained by addition of an ethylene oxide to a specific unsaturated alcohol, such as 3-methyl-3-buten-1-ol, an unsaturated carboxylic acid monomer and a monomer copolymerizable with these, or salts thereof as described in Japanese Kokai Publication Sho-62-68806 or like polycarboxylic acids (or salts thereof).

[0113]

The cement admixture of the present invention can be used by adding to a cement composition such as a cement paste, a mortar and a concrete like the known cement admixture. Alternatively, the cement admixture of the present invention can be also used in a super high strength concrete. As the aforementioned cement composition, cement components containing cement, water, a fine filler and a crude filler which are conventionally used are preferable. Alternatively, cement compositions to which a fine

powder such as a fly ash, a blast furnace slag, silica fume and limestone is added may be used. The super high strength concrete means entity which is generally termed so in the field of cement composition, that is, a concrete in which its hardened product  
 5 has a strength equivalent to or higher than that of the previous concrete even when a ratio of water/cement is reduced. Examples thereof include a concrete having such workability that it does not affect on normal use even at a ratio of water/cement of 25% by weight, further 20% by weight or less, particularly 18% by  
 10 weight or less, particularly 14% by weight or less, particularly about 12% by weight, and in which its hardened product exhibits a compression strength of 60 N/mm<sup>2</sup> or more, further 80 N/mm<sup>2</sup> or more, still further 100 N/mm<sup>2</sup> or more, particularly 120 N/mm<sup>2</sup> or more, particularly 160 N/mm<sup>2</sup> or more, particularly 200 N/mm<sup>2</sup>  
 15 or more.  
 [0114]

As the aforementioned cement, a portland cement such as normal, high early strength, super high early strength, moderate heat and white cements; a mixed portland cement such as an alumina  
 20 cement, a fly ash cement, a blast furnace cement and a silica cement are preferable. For example, in order to prepare a concrete having high durability and high strength, a blending amount and a unit water amount of the cement per 1 m<sup>3</sup> of a concrete is preferably a unit water amount of 100 to 185 kg/m<sup>3</sup> and  
 25 water/cement ratio = 10 to 70%. More preferably, a unit water amount is 120 to 175 kg/m<sup>3</sup>, and a water/cement ratio is 20 to 65%.  
 [0115]

A ratio of an addition amount of the cement admixture of  
 30 the present invention in a cement composition is preferably such that a polycarboxylic acid copolymer is preferably 0.01% by weight or more, and preferably 10% by weight or less relative to a total amount of 100% by weight of cement weight. When the ratio is smaller than 0.01% by weight, there is a possibility  
 35 that performance is insufficient. When the ratio exceeds 10%

by weight, economic property is inferior. The ratio is more preferably 0.05% by weight or more and 8% by weight or less, and still more preferably 0.1 by weight or more, and 5% by weight or less. The % by weight is a value in terms of a solid content.

5 [Effect of the Invention]  
[0116]

The cement admixture of the present invention has the aforementioned essential features, improves water-reducing property of a cement composition such as a cement paste, a mortar  
10 and a concrete, makes a strength and durability of its hardened product excellent, enhances slump-retaining ability of a cement component to maintain fluidity and, moreover, can realize such a viscosity that work is easy in a field handling it. Therefore, since the cement admixture of the present invention can improve  
15 work efficacy in constructing a civil engineering and construction structure excellent in fundamental performance, a hardened cement excellent in a strength and durability can be effectively formed and prepared.

[Best Mode for Carrying out the Invention]  
20 [0117]

The following examples illustrate the present invention more specifically. They are, however, by no means limitative of the scope of the invention. In the examples, "part(s)" means "part(s) by weight" and "%" denotes "% by weight", unless  
25 otherwise specified.

[0118]

[GPC molecular weight measurement conditions]

Column used: Tosoh TSK guard column SWXL + TSK gel G4000SWXL + G3000SWXL + G2000SWXL

30 Eluent: Sodium acetate trihydrate (115.6 g) is dissolved in a mixed solvent composed of 10,999 g of water and 6,001 g of acetonitrile, and the solution is further adjusted to pH 6.0 with acetic acid and used as the solution of the eluent.

Injection volume: 100  $\mu$ L of the 0.5% solution of the eluent



Eluent flow rate: 0.8 mL/min

Column temperature: 40°C

Standard samples: Polyethylene glycol, peak-top molecular weights (Mp) 272,500, 219,300, 85,000, 46,000, 24,000, 12,600, 4,250, 7,100, 1,470

Order of Calibration curve: 3rd-order

Detector: Waters, Japan's 410 differential refractive index detector

Analysis software: Waters, Japan's MILLENNIUM Ver. 3.21

[0119]

Production Example 1

(Production of  $H-(OC_2H_4)_{13}-(OC_3H_5)_2-(OC_2H_4)_{10}-OCH_3$ )

A reaction apparatus equipped with a thermometer, stirrer, raw material inlet tube and nitrogen inlet tube (nitrogen introducing tube) was charged with 1100 g of polyethylene glycol ( $n = 10$ ) monomethyl ether and 0.5 g of potassium hydroxide. The reaction vessel inside was purged with nitrogen, and heated to 120°C. While maintaining this temperature, 235 g of propylene oxide was added over 3 hours. After the addition, the reaction solution was matured at 120°C for 2 hours, and the reaction vessel was again purged with nitrogen and at 120°C. Then, 1165 g of ethylene oxide was added over 3 hours. After the addition, the reaction solution was further aged at 120°C for 1 hour to obtain alkylene glycol monomethyl ether with a hydroxyl value of 48 mg·KOH/g.

[0120]

Production Example 2

(Preparation of esterified product (a))

A reaction vessel equipped with a thermometer, stirrer, nitrogen inlet tube and condensation water separating tube was charged with 2083 g of polyalkylene glycol monomethyl ether obtained in Production Example 1, 350 g of methacrylic acid, 54 g of paratoluenesulfonic acid monohydrate, 0.5 g of phenothiazine and 243 g of cyclohexane as an azeotropic solvent, and esterification was performed by heating for 28 hours while

maintaining at 115°C to separate condensation water. At an esterification efficiency of 99% (conversion rate of polyalkylene glycol monomethyl ether), 510 g of distilled water and 41 g of a 30% sodium hydroxide solution were added. Then  
5 the reaction vessel was heated again to remove cyclohexane by azeotropy, and distilled water was added to obtain an aqueous solution of a mixture containing 72% of an esterified product (a) and 8% of unreacted methacrylic acid.

[0121]

#### 10 Production Example 3

A reaction vessel equipped with a thermometer, stirrer, dropping device, nitrogen inlet tube and reflux condenser (cooling tube) was charged with 50 g of distilled water, and the contents were heated to 80°C. Subsequently, a solution  
15 obtained by mixing 200.0 g of an aqueous solution of the mixture of the esterified product (a) and methacrylic acid obtained in Production Example 2, 25.2 g of methacrylic acid, 71.3 g of distilled water and 3.5 g of 3-mercaptopropionic acid was added dropwise over 4 hours, and a solution obtained by mixing 47.9  
20 g of distilled water and 2.1 g of ammonium persulfate was added dropwise over 5 hours. Thereafter, aging was performed for 1 hour while maintaining at 80°C, then the mixture was cooled, a 30% aqueous sodium hydroxide solution was added to adjust a pH to 7, and distilled water was further added to obtain a copolymer  
25 (A) containing 75% of the site derived from an esterified product (a) with a weight average molecular weight of 14,000. A composition and a weight average molecular weight of a copolymer (A) are shown in Table 1.

[0122]

#### 30 Production Example 4

A reaction vessel equipped with a thermometer, stirrer, a dropping device, nitrogen inlet tube and reflux condenser was charged with 50 g of distilled water, and the contents were heated to 80°C. Subsequently, a solution obtained by mixing 211.1 g  
35 of an aqueous solution of the mixture of the esterified product

(a) and methacrylic acid obtained in Production Example 2, 16.6 g of methacrylic acid, 69.8 g of distilled water and 2.5 g of 3-mercaptopropionic acid was added dropwise over 4 hours, and a solution obtained by mixing 47.9 g of distilled water and 2.1 g of ammonium persulfate was added dropwise over 5 hours. Thereafter, aging was performed for 1 hour while maintaining at 80°C, then the material was cooled, a 30% aqueous sodium hydroxide solution was added to adjust a pH to 7, and distilled water was further added to obtain a copolymer (B) containing 80% of the site derived from the esterified product (a) with a weight average molecular weight of 18,000. A composition and a weight average molecular weight of a copolymer (B) are shown in Table 1.

[0123]

#### 15 Production Example 5

A reaction vessel equipped with a thermometer, stirrer, dropping device, nitrogen inlet tube and reflux condenser was charged with 60 g of distilled water, and the contents were heated to 80°C. Subsequently, a solution obtained by mixing 230.4 g of an aqueous solution of the mixture of the esterified product (a) and methacrylic acid obtained in Production Example 2, 1.6 g of methacrylic acid, 4.0 g of distilled water, 1.3 g of a 30% aqueous sodium hydroxide solution, and 2.7 g of 3-mercaptopropionic acid was added dropwise over 4 hours, and a solution obtained by mixing 49.1 g of distilled water and 0.87 g of a 30% aqueous hydrogen peroxide solution, and a solution obtained by mixing 49.7 g of distilled water and 0.34 g of L-ascorbic acid were added dropwise for 5 hours, respectively. Thereafter, aging was performed for 1 hour while maintaining at 80°C, then the mixture was cooled, a 30% aqueous sodium hydroxide solution was added to adjust a pH to 7, and distilled water was further added to obtain a copolymer (C) containing 89% of the site derived from the esterified product (a) a weight average molecular weight of 11,000. A composition and a weight average molecular weight of a copolymer (C) are shown in Table

1.

[0124]

Production Example 6

(Preparation of esterified product (b))

5       A reaction vessel equipped with a thermometer, stirrer, nitrogen inlet tube and condensation water separating tube was charged with 2033 g of polyethylene glycol ( $n = 25$ ) monomethyl ether, 400 g of methacrylic acid, 54 g of paratoluenesulfonic acid monohydrate, 0.5 g of phenothiazine and 243 g of cyclohexane  
10 as an azeotropic solvent, and esterification was performed by heating for 20 hours at 115°C separating condensation water. At an esterification efficiency of 99% (conversion rate of polyethylene glycol monomethyl ether), 509 g of distilled water and 42 g of a 30% sodium hydroxide solution were added. Then  
15 the reaction vessel was heated again to remove cyclohexane by azeotropy, and distilled water was added to obtain an aqueous solution of a mixture containing the esterified product (b) at 70% and unreacted methacrylic acid at 10%.

[0125]

20   Production Example 7.

      A reaction vessel equipped with a thermometer, stirrer, dropping device, nitrogen inlet tube and reflux condenser was charged with 50 g of distilled water, and the contents were heated to 80°C. Subsequently, a solution obtained by mixing 215.9 g  
25 of aqueous solution of the mixture of the esterified product (b) and methacrylic acid obtained in Production Example 6, 12.8 g of methacrylic acid, 69.8 g of distilled water and 1.5 g of 3-mercaptopropionic acid was added dropwise over 4 hours, and a solution obtained by mixing 47.9 g of distilled water and 2.1  
30 g of ammonium persulfate was added dropwise over 5 hours. Thereafter, aging was performed for 1 hour while maintaining at 80°C, then the mixture was cooled, a 30% aqueous sodium hydroxide solution was added to adjust a pH to 7, and distilled water was further added to obtain a copolymer (D) containing  
35 80% of the site derived from the esterified product (b) with

a weight average molecular weight of 22,000. A composition and a weight average molecular weight of a copolymer (D) are shown in Table 1.

[0126]

#### 5 Production Example 8

A reaction vessel equipped with a thermometer, stirrer, addition apparatus, nitrogen inlet tube and reflux condenser was charged with 50 g of distilled water, and the contents were heated to 80°C. Subsequently, a solution obtained by mixing  
 10 232.5 g of an aqueous solution of the mixture of the esterified product (b) and methacrylic acid obtained in Production Example 6, 66.5 g of distilled water and 1.1 g of 3-mercaptopropionic acid was added dropwise over 4 hours, and a solution obtained by mixing 47.9 g of distilled water and 2.1 g of ammonium persulfate  
 15 was added dropwise over 5 hours. Thereafter, aging was performed for 1 hour while maintaining at 80°C, then the material was cooled, a 30% aqueous sodium hydroxide solution was added to adjust a pH to 7, and distilled water was further added to obtain a copolymer (E) containing 87.5% of the site derived from the esterified  
 20 product (b) with a weight average molecular weight of 22,000. A composition and a weight average molecular weight of a copolymer (E) are shown in Table 1.

[0127]

[Table 1]

Polymer	Composition (ratio by mass)	Molecular weight (Mw)
(A)	PGM-10E2P13E/SMAA=75/25	14000
(B)	PGM-10E2P13E/SMAA=80/20	18000
(C)	PGM-10E2P13E/SMAA=89/11	11000
(D)	PGM-25E/SMAA=80/20	22000
25 (E)	PGM-25E/SMAA=87.5/12.5	22000

[0128]

In Table 1, "PGM-10E2P13E" is an ester compound (a), and "PGM-25E" is an ester compound (b).

[0129]

Examples 1 and 2, and Comparative Example 1

Copolymers (A) to (E) obtained in Production Examples were mixed at a ratio indicated in Table 2, and the mixture was assessed by a concrete test method as follows. Results are shown in Table 2. An addition amount represents % by weight of a solid content in an admixture relative to cement weight, and a mixing ratio of an admixture represents a weight ratio of a solid content.

[0130]

[Concrete test]

Concrete formulation was conducted following composition.

Water: 172kg/m<sup>3</sup>

Cement (Ordinary portland cement : product of Taiheiyo Cement, Sumitomo Osaka Cement, Ube Mitsubishi Cement) : 491kg/ m<sup>3</sup>

Fine aggregate (Ohigawa river sand): 744.6kg/ m<sup>3</sup>

Coarse aggregate (Oume crushed stone): 909.8kg/ m<sup>3</sup>

W/C: 35%

Under the above-mentioned formulation, cement admixture is mixed by mixing water in advance, 30L of concrete ingredient were charged to a 50L forced action mixer and mixed for 60 seconds.

The concrete obtained was measured for slump flow value and air amount according to the Japanese Industrial Standards (JIS A 1101, 1128, and 6204).

[0131]

[Method of measuring flow stop value]

A flow stop value was obtained by measuring a time that the flow stopped when the aforementioned initial (0 min) slump flow value was measured.

[0132]

[Table 2]

	Cement admixture	Addition amount (%)	Slump flow value (mm)			Flow stop value (sec)	Air amount (%)	Concrete state
			0(min)	30(min)	60(min)			
Example 1	(A)/(C)=2/8	0.26	493	420	378	13.3	3.8	○
Example 2	(B)/(C)=2/8	0.24	500	445	415	13.8	3.2	○
Comparative Example 1	(D)/(E)=2/8	0.24	510	455	420	16.5	3.7	×

[0133]

5 The condition of a concrete in Table 2 indicates feeling when a concrete was mixed by a scoop, and the better condition of light and smooth feeling is indicated by ◎, and the worse condition of heavy and sticky feeling is indicated by ×. When a concrete is in the lighter and smoother condition, it is an easily handled concrete.